December 1955 Pages 697-760

The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 71 Number 12

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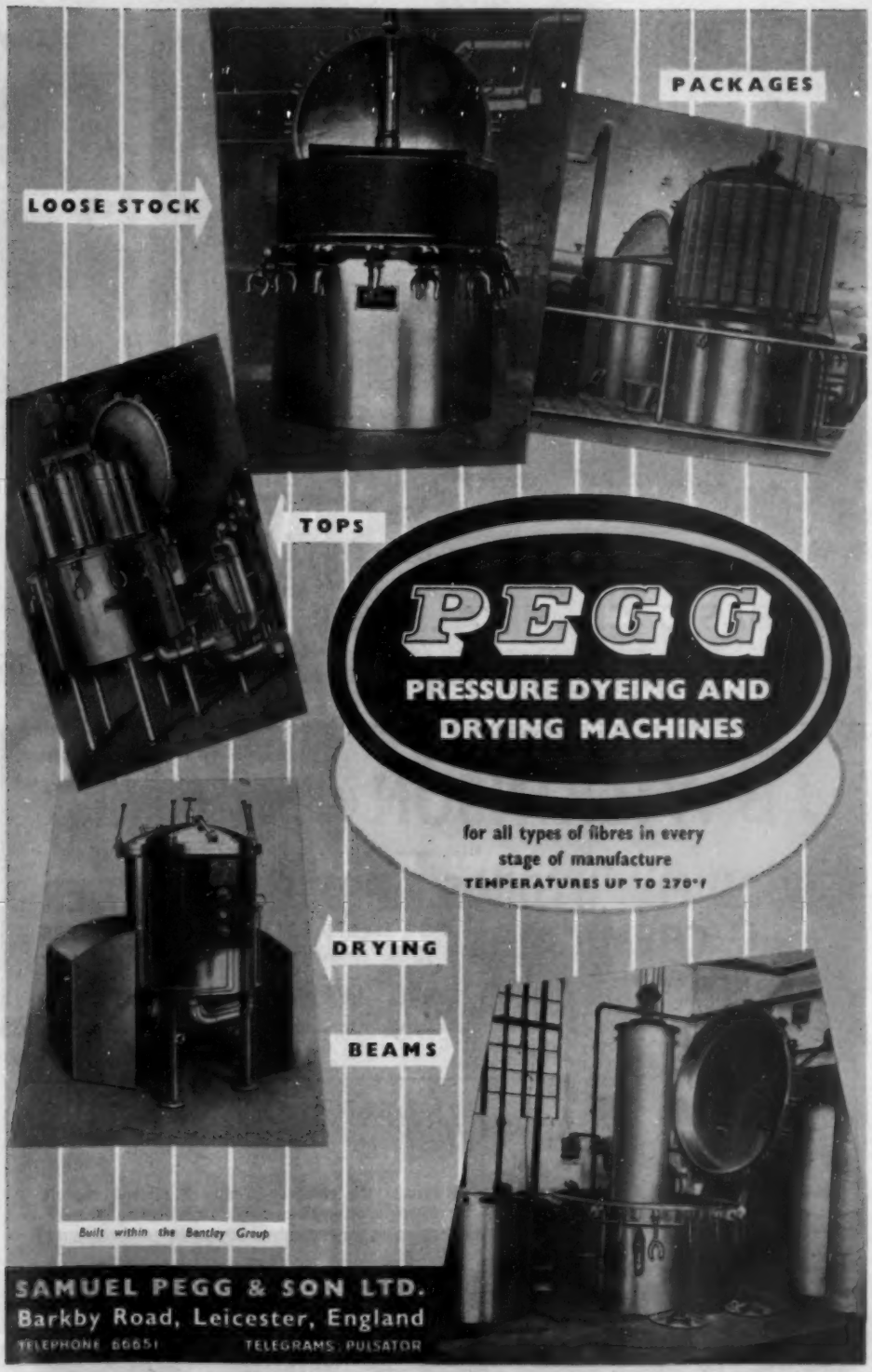
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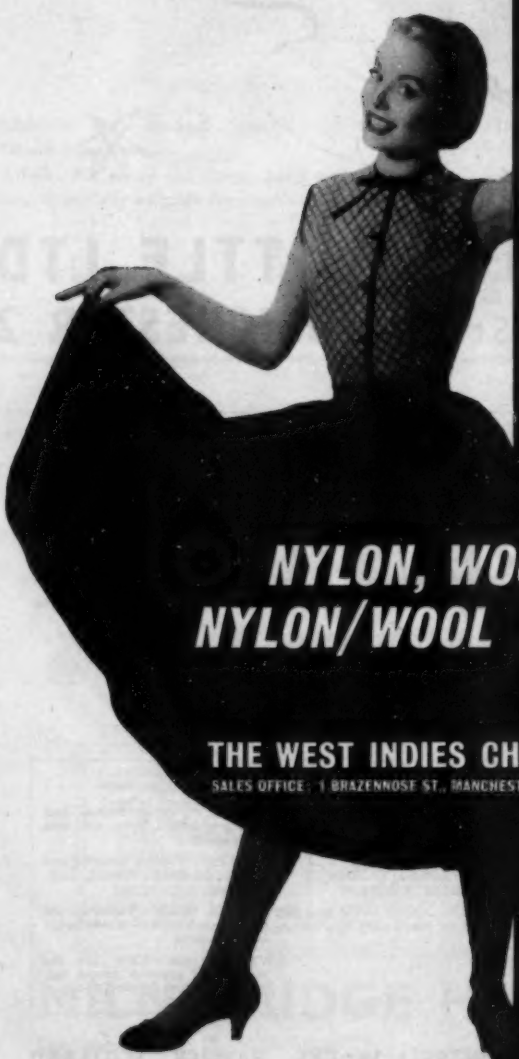

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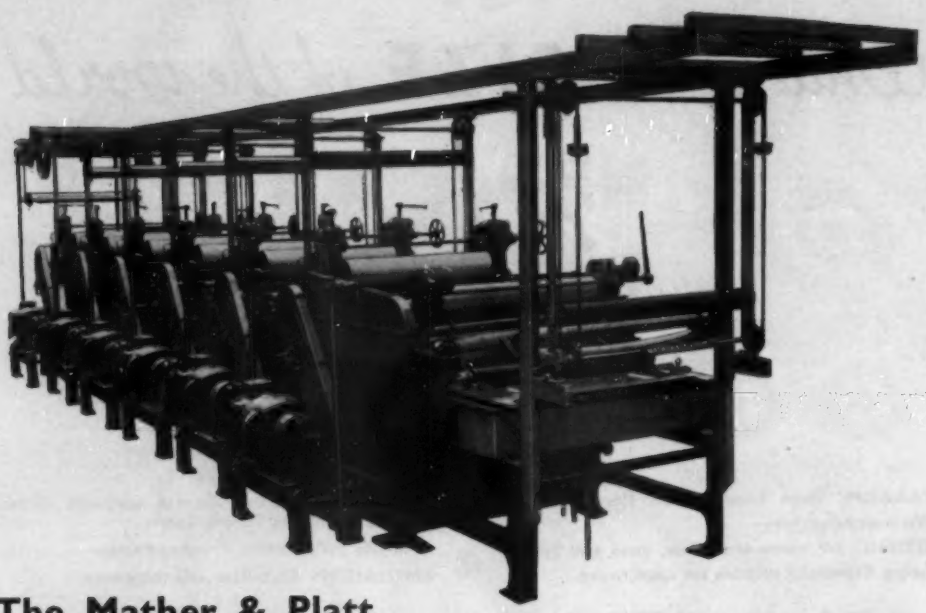

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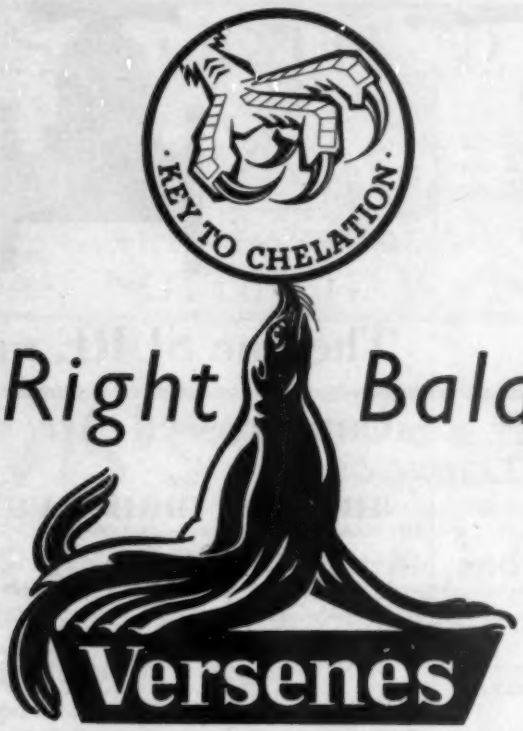

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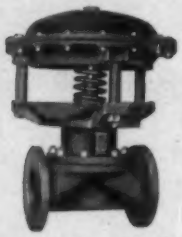

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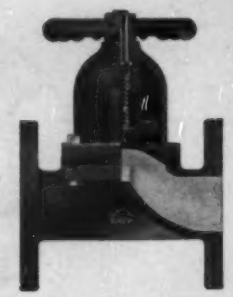

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1955 and pages 369–373 of the July 1955 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal* —

LECTURES

Some Observations on American Bleaching and Dyeing Processes	*J. K. Skelly*
The Dyeing and Finishing of Nylon Ribbons	*W. S. Willson*

F.T.C.C. PUBLICATION

The Spectral Regions of Daylight which cause Fading	*K. McLaren*

COMMUNICATIONS

The Polarography of Azo Dyes	*J. de O. Cabral and H. A. Turner*
The Dyeing of Cellulose Acetate with Non-ionic Dyes III—Dyeing from the Vapour Phase	*T. G. Majury*
The Combination of Wool with Acids	*B. Olofsson*

THE SOCIETY OF DYERS AND COLOURISTS

ASSOCIATESHIP EXAMINATIONS 1956

The next Associateship Examinations will be held on **Thursday, Friday and Saturday, 14, 15 and 16 June 1956.**
Closing date for receipt of candidates' applications **31 March 1956**

THE
THIRTEENTH MERCER LECTURE
will be held in
Glasgow on **Friday 13th April 1956**
Mr R. K. FOURNESS
B.Sc F.R.I.C F.S.D.C
will lecture on Disperse Dyes

THE
FOURTH LONDON LECTURE
will be held on **Friday 20th April 1956**
at the **Waldorf Hotel, London, W C 2**
at 7 p m
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FORTHCOMING MEETINGS OF THE SOCIETY

Wednesday, 11th January 1956

NORTHERN IRELAND SECTION. *Causes of Felting in Rayon Textiles.* H. W. Best-Gordon, Esq. (Courtaulds Ltd.). (Joint Meeting with the Textile Institute), Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 12th January 1955

WEST RIDING SECTION. *User Dyer Relations.* I. Glasman, Esq., A.T.I. (Marks & Spencer Limited). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 13th January 1956

BRADFORD JUNIOR BRANCH. Lecture Title to be announced later. Midland Silicones Ltd. Technical College, **Bradford.** 7.15 p.m.

LONDON SECTION. *The Use of Old Documents in Modern Printing.* Ronald Baker, Esq. (Swaislands Fabric Printing Company). Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

Tuesday, 17th January 1956

HUDDERSFIELD SECTION. Title later. Professor J. B. Speakman.

SCOTTISH SECTION. *What Dyeing does to Wool.* F. F. Elsworth, Esq., Ph.D., A.R.I.C., F.S.D.C. (Wool Industries Research Association). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 18th January 1956

MIDLANDS SECTION. Discussion Group on *Detergency.* Questions invited. G. H. Rostron, Esq., A.R.I.C. (Soap), R. C. Tarring, Esq., B.Sc., A.R.C.S. (Synthetics), and R. S. Hartley, Esq., A.R.I.C. (Research). Kings Head Hotel, **Loughborough.** 7 p.m.

Friday, 20th January 1956

MANCHESTER SECTION. *The Finishing of 'Terylene' Polyester Fibre Staple and Filament Fabrics.* G. D. Myers, Esq., B.Sc.Tech. Textile Institute, 10 Blackfriars Street, **Manchester 10.** 6.30 p.m.

LONDON SECTION. Perkin Centenary Dinner Dance. Waldorf Hotel, **London, W.C.2.** 7 p.m.

WEST RIDING SECTION. Ladies' Evening. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Tuesday, 24th January 1956

LEEDS JUNIOR BRANCH. *Fading — Its Nature and Assessment.* H. B. Mann, Esq. (Messrs. Courtaulds Ltd.). The Lecture Theatre, Department of Colour Chemistry and Dyeing, The University, **Leeds 2.** 3.30 p.m.

Thursday, 26th January 1956

WEST RIDING SECTION. *Textile Invention and the Dry Cleaner.* A. J. Crockatt, Esq., M.Sc., F.R.I.C. (Messrs. Eastmans). The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Monday, 30th January 1956

BRADFORD JUNIOR BRANCH. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Coventry Ltd.). Technical College, **Bradford.** 7.15 p.m.

Thursday, 2nd February 1956

SCOTTISH SECTION. *Scouring and Milling.* B. F. J. Moxon, Esq. (Wool Industries Research Association). The Scottish Woollen Technical College, **Galashiels.** 7 p.m.

Friday, 3rd February 1956

LONDON SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Ltd., Coventry). Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

Tuesday, 7th February 1956

LEEDS JUNIOR BRANCH. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Messrs. Courtaulds Ltd.). The Lecture Theatre, Department of Colour Chemistry and Dyeing, The University, **Leeds 2.** 3.30 p.m.

Wednesday, 8th February 1956

NORTHERN IRELAND SECTION. *General Principles in Vat Dyeing.* J. W. Reidy, Esq. (Messrs. L. B. Holliday & Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 9th February 1956

WEST RIDING SECTION. *The Dyeing and Finishing of 'Terylene' and 'Terylene'/Wool Blended Fabrics.* H. R. Hadfield, Esq., M.Sc.Tech. and G. D. Myers, Esq., M.Sc.Tech. (Imperial Chemical Industries Limited, Dyestuffs Div., and Terylene Council). The Victoria Hotel, Bridge Street, Bradford. 7.30 p.m.

Tuesday, 14th February 1956

SCOTTISH SECTION. *The Dyeing and Finishing of 'Terylene' and 'Terylene' Blends.* J. G. Graham, Esq., and Dr. P. T. Standring (I.C.I. 'Terylene' Council). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 15th February 1956

BRADFORD JUNIOR BRANCH. *Piece Scouring.* B. F. J. Moxon, Esq. (Wool Industries Research Association). Technical College, **Bradford.** 7.15 p.m.

Friday, 17th February 1956

MANCHESTER SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq., B.Sc. Textile Institute, 10 Blackfriars Street, **Manchester 10.** 6.30 p.m.

NORTHERN IRELAND SECTION. Dinner Dance. Details later, at Woodbourne House Hotel.

Saturday, 18th February 1956

MANCHESTER SECTION. Perkin Centenary Ball. It is proposed to hold a Dinner Dance at the Midland Hotel, Manchester on this date.

Monday, 20th February 1956

HUDDERSFIELD SECTION. *The Finishing of 'Terylene' and 'Terylene' Wool Blended Fabrics.* N. M. Mims, Esq., B.A., B.Sc. (Joint Lecture with the Huddersfield Textile Society). Large Hall, Technical College, **Huddersfield.** 7.30 p.m.

Thursday, 23rd February 1956

MIDLANDS SECTION. *The Finishing of 'Terylene' and 'Terylene'/Wool Blends.* I. E. Haden, Esq., B.Sc., and B. I. Brooke, Esq., B.A.(Oxon.). Gas Theatre, **Nottingham.** 7 p.m.

NORTHERN IRELAND SECTION. *Film Evening.* Thompson's Restaurant, Donegall Place, **Belfast.** (Joint Meeting with the Textile Institute.) 7.30 p.m.

WEST RIDING SECTION. *Progress in the Cibalan Dye Range and their Application.* Clayton Dyestuffs Co. Ltd. Lecturer details later. The Victorial Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 2nd March 1956

LONDON SECTION. *Basic Mechanisms of Fading of Dyed Textiles.* H. B. Mann, Esq. (Courtaulds Ltd., Bocking). Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

BRADFORD JUNIOR BRANCH. Annual Dance. Connaught Rooms, **Bradford.**

Tuesday, 6th March 1956

LEEDS JUNIOR BRANCH. *The Textile Technologist in the Hosiery Trade.* F. M. Stevenson, Esq., M.Sc., J.P. (Messrs. Stevensons (Dyers) Ltd., Ambergate, Derbyshire). The Lecture Theatre, Department of Colour Chemistry and Dyeing, The University, **Leeds 2.** 3.30 p.m.

Thursday, 8th March 1956

WEST RIDING SECTION. *A Commentary on the Use of Colour in Wool.* S. Morse-Brown, Esq. International Wool Secretariat. Ladies to be invited. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 9th March 1956

MIDLANDS SECTION. Midlands Section Dinner. Bull's Head Hotel, **Loughborough.**

Tuesday, 13th March 1956

SCOTTISH SECTION. *The Soiling of Synthetic Fibres.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). St. Enoch's Hotel, **Glasgow.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Some Aspects of Continuous Vat Dyeing.* Dr. R. J. Rallings (British Cotton Industries Research Association). Technical College, **Bradford.** 7.15 p.m.

Wednesday, 14th March 1956

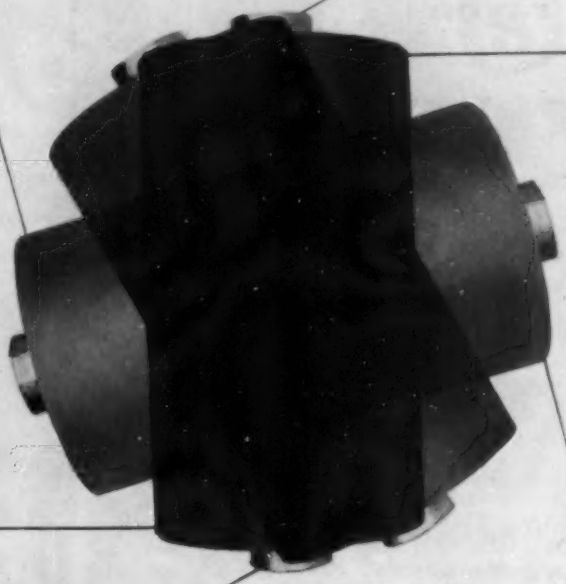
NORTHERN IRELAND SECTION. *Various Methods of Stripping Vat, Azoic, Direct and Sulphur Dyes.* J. E. Riordan, Esq. (College of Technology, Belfast.) *Effect of pH on the Activity of Bleaching Agents.* J. Boyd, Esq. (College of Technology, Belfast). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Tuesday, 20th March 1956

HUDDERSFIELD SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Ltd.). Co-operative Cafe, **Huddersfield.** 7.30 p.m.

continued on page xxxiii

Colours for Nylon and other Synthetic Fibres



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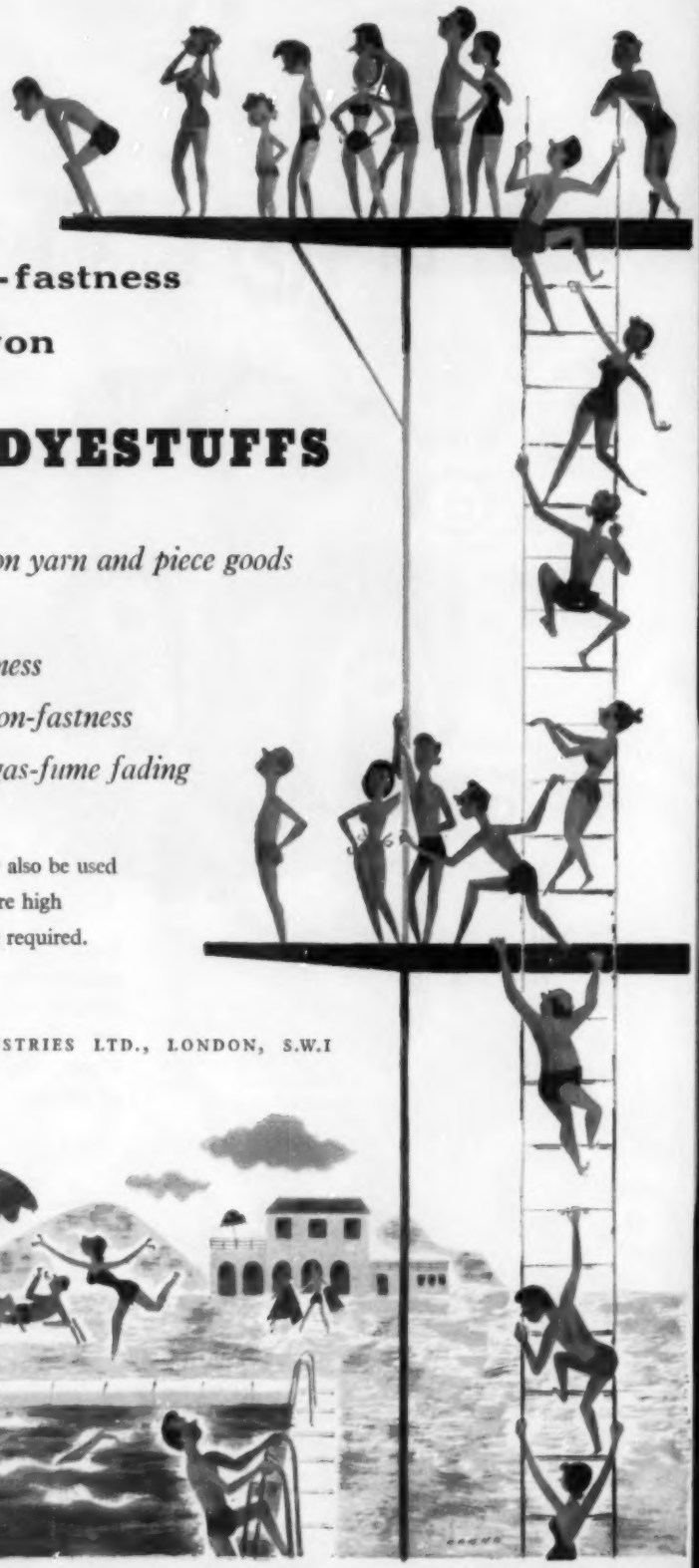

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OF THE

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Volume 71 Number 12 DECEMBER 1955 *Issued Monthly*

Proceedings of the Society

Estimation of Fluorescent Brightening Agents

G. G. Taylor

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The present paper is limited to comparative strength determination of chemically identical samples. The problems are closely analogous to those of the strength determination of dyes, the differences arising mainly from the nature of the light source and the small amount of fluorescent light available. Particular difficulties, such as the *cis–trans* isomerism of stilbene derivatives, are more prominent with fluorescent brightening agents than with dyes.

Strength determination in solution is necessarily limited to instrumental methods. The Spekker (Hilger) fluorimeter is discussed in detail and the method of converting the readings to a function analogous to optical density is given.

For strength determination on a substrate, both visual and instrumental methods are discussed. The accuracy of visual estimation is comparatively low but may be considerably improved by a technique analogous to "cross-dyeing" in dye estimation. No commercial instruments for measurement on substrates exist, but a simple adaptation of the Spekker fluorimeter is described which gives useful results within its limitations.

Introduction

During the past few years the use of fluorescent brightening agents in textile finishing and in detergents has become widespread, and although they are never likely to be used in the same quantities as dyes, strength determination of commercial production has become a matter of some importance. The purpose of this paper is to consider the available methods of estimation. Discussion of properties, and of methods of application, is specifically excluded, except insofar as these are relevant to the question of determination.

Fluorescent brightening agents may be regarded as in many ways similar to dyes, but their mode of action is exactly opposite. Whereas a blue dye obtains its colour by removing light from the yellow region of the spectrum, a fluorescent brightening agent obtains its blue colour by adding light to the blue region. It does this by borrowing invisible ultraviolet radiation and converting it into visible blue light. From the dyer's point of view the general effect is similar: the more dye or fluorescent brightening agent that is added, the bluer the material becomes, and in both cases a limiting value is reached. With the dye, the limit is reached when all the yellow light has been absorbed. With the fluorescent brightening agent, this occurs when all the available ultraviolet radiation has been converted into blue light.

It is natural, therefore, that the problems of strength determination on fluorescent brightening agents should be closely parallel to those on normal dyes. The latter are well known, and will merely be briefly enumerated here in order to emphasise this parallelism.

The method of evaluation of a product should be related as closely as practicable to its intended use. This is a general principle which applies to any product, but which in practice is difficult to follow faithfully. The majority of fluorescent brightening agents are intended for application to textiles, and strength estimations should, therefore, be made on the appropriate substrate; the same applies, of course, to dyes. It is generally accepted, however, that satisfactory strength measurements on dyes cannot be made with simple instruments. A spectrophotometer of adequate accuracy is a complex instrument costing some hundreds or thousands of pounds, depending on the extent to which its operation is automatic. Additionally, the figures or graphs which it produces require some experience to interpret in practical terms. The requirements for an instrument for testing fluorescent brightening agents are roughly the same, apart from minor technical difficulties connected with the ultraviolet source.

It follows that the majority of dyehouses wishing to make estimations on fluorescent brightening agents will have to accept simpler

testing methods. As with dyes, these will consist in instrumental measurements on solutions or visual measurements on textiles. The third and simplest method used with dyes—visual comparison of solutions—has several difficulties, which will be mentioned when solution-measuring instruments are discussed, and it does not appear to be very suitable.

Strength Measurements on Solutions

The accuracy and the reproducibility of a dye solution are greater than those of a dyed textile, because, whilst both are subject to errors of weighing and volumetric measurement, the textile has the additional dyeing variations of penetration and levelness. The accuracy with which a solution of a fluorescent brightening agent can be made up is less than in the case of a dye, simply because the test solution is required to be very dilute, and two or three successive dilutions are necessary to reach the desired concentration, whereas one will suffice for a colorimetric solution of a dye. These volumetric errors should, however, be quite small if the work is carried out with normal care. In addition, there is obviously a greater danger of contamination of very dilute solutions, particularly as the solutions are colourless under normal laboratory lighting, and contamination from traces of stronger solutions or solid material cannot be seen. When we began testing fluorescent brightening agents, all our volumetric work was done in a darkroom under a "black" ultraviolet lamp, in order that contamination might be seen. It was soon found, however, that this precaution was quite unnecessary. Those of the brightening agents which are soluble in water are in fact readily soluble and have no tendency to adhere to glass, so that it is sufficient to wash all volumetric apparatus thoroughly as soon as it has been used.

Although water is the most common solvent in colorimetric work, certain fluorescent brightening agents intended for use in detergent powders are insoluble in water, and another solvent must be used. Generally they are soluble in ethyl alcohol (in the form of industrial methylated spirits) or other common organic solvent.

Even if a particular brightening agent is soluble in a certain solvent, it will not necessarily be fluorescent. Several water-soluble products show little or no fluorescence in water. In the majority of cases satisfactory fluorescence is obtained in ethyl alcohol, while in others Cellosolve must be used. For one or two products, no suitable solvent has so far been found. It is not sufficient, of course, for a solvent simply to yield a fluorescent solution: it must also be available in considerable quantities at reasonable cost, and must satisfy the usual requirements of non-toxicity and safety of handling. Miscibility with water, or at any rate with alcohol or acetone, is also an advantage, to facilitate cleaning of apparatus.

Some industrial grades of solvents are themselves fluorescent, possibly owing to the presence of traces of oil. This fluorescence can generally be eliminated, or at least reduced, by distillation, but the distillation of large quantities of liquid greatly adds to the general inconvenience of using solvents. In the Hilger fluorimeter correction may be made for the fluorescence of the solvent, but if this is comparable with that of the solution of brightening agent, there will inevitably be a reduction in accuracy.

No attempt should be made to obtain even a rough comparison of the fluorescence of brightening agents which are not chemically similar, in water or any other solvent. The fluorescence of a product in solution gives no reliable indication of its fluorescence when adsorbed on the substrate for which it is intended.

INSTRUMENTS FOR MEASUREMENTS ON SOLUTIONS

The general design of instruments for measurements on fluorescent solutions shows large differences from that of colorimeters for the visible region. In the latter, an intense and well defined beam of light is passed through the dye solution, and the intensity of the transmitted light is measured either visually or by means of a photocell. In the fluorescence instrument, a beam of ultraviolet radiation is passed into the cell, where it is converted into visible radiation, which is scattered in all directions. In the case of brightening agents there is apparently a sufficiently long interval between the absorption of a quantum of ultraviolet radiation and the emission of a quantum of blue light for the absorbing molecule to re-orientate itself randomly, so that the fluorescence is emitted more or less equally in all directions. The distribution of fluorescence is not, however, uniform throughout the cell. The ultraviolet beam is absorbed exponentially as it passes through the cell, and the fluorescence is therefore strongest at the point of entry of the beam and decreases towards the point of exit. This non-uniformity, together with the fact that the fluorescence is generally rather weak, makes difficult the design of an accurate visual fluorescence-measuring instrument.

The distribution of the fluorescence requires careful consideration also in designing the optics of a photoelectric instrument. The most obvious method is to place the solution cell at the centre of an integrating sphere, with the photocell in line with the ultraviolet beam, behind the shield used to absorb the surplus ultraviolet radiation which has passed through the solution. This construction has obvious complications, and in the most widely used commercial instrument, the Spekker fluorimeter, a simpler construction is adopted which, although much less satisfactory from the theoretical point of view, in practice works better than might at first sight appear.

The Spekker Fluorimeter (Hilger & Watts)

The Spekker fluorimeter is a modification of the Spekker absorptiometer as used for colorimetry in the visible range: the two instruments may in fact be interchanged by exchanging lamps and cell-holders. The light source is a mercury-vapour discharge lamp, the visible light being removed by

"black" Woods-glass filters, leaving only ultraviolet of 3670 A. The left-hand side of the instrument contains filter-holders, diaphragms, and a photocell. On the right-hand side the ultraviolet beam, after passing through filter-holders and a calibrated diaphragm, is deflected vertically upwards by a mirror, through the base of the solution cell; the latter has a black glass top to absorb the ultraviolet radiation which passes through the cell. Photocells are placed on each side of the solution-cell (Fig. 1). The photocells obviously collect only a small fraction of the total fluorescent emission, but this is adequate in the case of most brightening agents. There is no apparent reason for the rather peculiar geometry adopted. The photocells are placed some distance from the solution-cell, whereas it would seem better to place them as close as possible, and there is no evident reason against doing so. Even more peculiar is the fact that the photocells are placed higher than the solution-cell, although the strongest fluorescence is from the bottom of the cell. This construction affects the results obtained

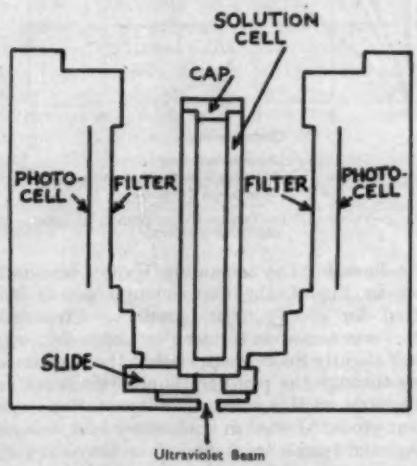


FIG. 1—Cross-section of Fluorimeter

to a considerable extent. The two right-hand photocells are connected together in parallel, and in opposition to the left-hand photocell, across a galvanometer. The latter is more sensitive than that used on the Spekker absorptiometer, being of the lamp-and-scale type. A modification has recently been introduced in which only one photocell is used on the right-hand side, this being of the electron-multiplier type giving increased sensitivity. This is useful for the measurement of very weak fluorescence, but for brightening agents the older arrangement is generally adequate.

The method of use is as follows: with the sample solution in the right-hand beam, and the right-hand diaphragm fully open, the instrument is balanced by means of the left-hand diaphragms. A much stronger solution is then substituted for the sample; the exact strength is unimportant, 5–10 times the concentration of the sample being generally suitable. The instrument is again balanced, by means of the right-hand diaphragm. The drum which controls this diaphragm has two scales, of optical density and percentage transmission. It is the latter which is most useful for fluorescence measurements. It will be seen that the method of use is exactly analogous to that of the Spekker absorptiometer. The function of the "strong standard" solution is to convert *all* the available ultraviolet radiation into visible light: it plays exactly the same part as the cell containing solvent only in the use of the Spekker absorptiometer.

When the sample solution is in position, let the intensity of ultraviolet radiation entering the cell be I_0, and let I_h reach the top of the cell of height h. The fluorescent emission is proportional to the quantity of ultraviolet absorbed, viz. $(I_0 - I_h)$. Similarly, when the strong standard solution is in position, the fluorescent emission is proportional to—

$$\frac{DI_0}{100}$$

where D is the percentage opening of the diaphragm (all the ultraviolet radiation is absorbed before reaching the top of the cell). These two amounts of fluorescence are equal, as both have been balanced against the same setting of the left-hand side. Hence, for balance—

$$I_0 - I_h = \frac{DI_0}{100}$$

Also, Lambert's law of absorption applies—

$$I_h = I_0 e^{-ach}$$

where a is the absorption coefficient and c the concentration of the brightening agent. Combining these equations—

$$1 - \frac{D}{100} = e^{-ach}$$

Inverting—

$$e^{ach} = \frac{100}{100 - D}$$

Taking logarithms—

$$\begin{aligned} ach &= \ln\left(\frac{100}{100 - D}\right) \\ &= 2{\cdot}303 \log\left(\frac{100}{100 - D}\right) \\ &= 2{\cdot}303\,[2 - \log(100 - D)] \\ &= 2{\cdot}303\,T \end{aligned}$$

or—

$$T = \frac{ah}{2{\cdot}303}\,c$$

As $h = 4{\cdot}6$ cm.—

$$T = 2ac$$

If the solvent also is fluorescent, and has absorption coefficient s, the equation becomes—

$$(ac + s)h = 2{\cdot}303T$$

For pure solvent—

$$sh = 2{\cdot}303\ T_s$$

Hence—

$$ach = 2{\cdot}303\ (T - T_s)$$

or—

$$T - T_s = \frac{ach}{2{\cdot}303} = 2ac$$

In the foregoing theory it is assumed that the strong standard absorbs all the ultraviolet radiation which enters the cell. This is not the case, as absorption follows an exponential law, and some ultraviolet must reach the top of the cell. If the concentration of the strong standard is n times that of the sample, the balance equation becomes—

$$1 - e^{-ach} = \frac{D}{100}\ (1 - e^{-nach})$$

which can be solved only approximately.

By using a very strong standard solution the fraction of unabsorbed ultraviolet may be made extremely small, but unfortunately this leads to other troubles. The theory tacitly assumes that the photocells receive the same fraction of light from all parts of the solution-cell, and in view of the geometry of the system, already shown, this is obviously not the case. When a new brightening agent is to be tested, suitable concentrations must be found by trial, and it often happens that peculiar results are obtained, the sample appearing to be stronger than the strong standard. This is a sure sign that the solutions are much too concentrated, and both the sample and the strong standard should be diluted by a factor of 10 and another trial made. Values of the function T between 0·2 and 0·4 are generally suitable.

In view of these approximations it might be expected that only an approximately linear relation would exist between T and concentration. It is found in practice, however, that a very good straight line is obtained provided that T is less than 0·5. This must be ascribed to the fortunate balancing-out of sundry errors, rather than to any exactness of the simple theory given.

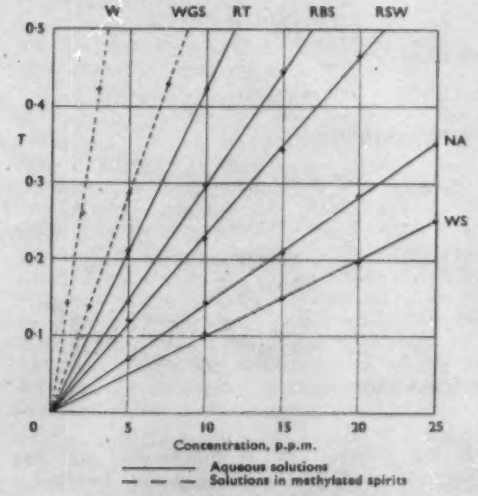


FIG. 2—Values of T for Various Uvitex Brands

The experimental points for several Uvitex (CDC) brands are shown in Fig. 2, from which it will be seen that the drawing of a straight line through them is quite justified. In all cases this passes through the origin, as water and industrial methylated spirits have no fluorescence of their own. The solvent is water except where otherwise stated.

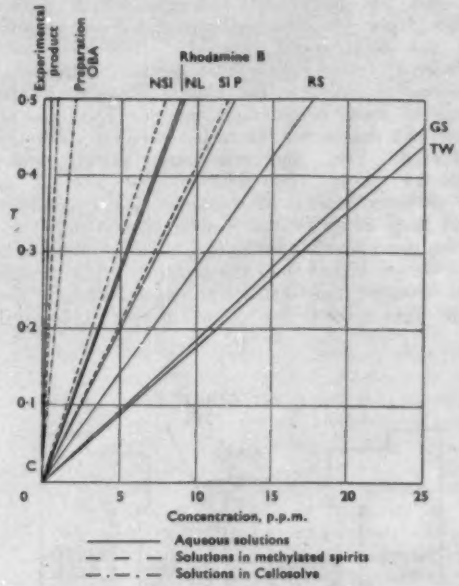


FIG. 3—Values of T for Various Uvitex Brands, Rhodamine B, and Other Products

The lines for the remaining Uvitex brands are shown in Fig. 3, the experimental points being omitted for clarity. One product—Preparation OBA—was tested in solution in Cellosolve, which is itself slightly fluorescent, so that the line actually passes through the point C, though this is not very conspicuous on this scale. The lines for an experimental product tested in both water and industrial methylated spirits are included, as they show that the gradient depends on the solvent. A fluorescent dye—Rhodamine B—is included as a matter of interest, to show that the same theory applies. As the solutions are extremely dilute, the absorption of the fluorescent emission due to the colour of the dye is negligible.

When once it has been established that a straight line is obtained for a particular compound, the estimation of the strength of an unknown sample is quite simple. The line may be determined once and for all by means of a set of standard solutions, and the position of the unknown sample found on this; a suitable dilution will have to be found by trial. In view of normal volumetric errors, however, it is more accurate to make up a known standard solution at the same time as the unknown, and determine the strength by simple proportion from the T values. One solution of each is sufficient, but to avoid the possibility of error it is preferable to make up two or three separate solutions of each.

It will be noted that the gradients of the lines of *T versus* concentration cover quite a wide range. The gradient is proportional to the absorption coefficient for ultraviolet radiation, but does not necessarily give any indication of the strength of fluorescence. In any case, the fluorescence in solution is unrelated to that on the intended substrate, so the gradient should not be taken as giving any indication of the relative strengths of different compounds. The gradient is mainly of interest from the theoretical point of view, in relating the absorption to the chemical structure.

It may be noted that, as the "fluorimeter" really only measures absorption coefficient, this could equally well be measured by a transmission instrument such as the Spekker absorptiometer, but, of course, using an ultraviolet source. Such an instrument would determine the absorption coefficient regardless of whether the compound was fluorescent.

One difficulty must be mentioned before leaving the subject of fluorimetry in solution. Quite a number of fluorescent brightening agents are stilbene derivatives, and show the same phenomenon of *cis–trans* isomerism as certain dyes. The equilibrium between the two forms of the molecule is affected by temperature and illumination, and after a change in these conditions it may take upwards of an hour before the solution reaches a new equilibrium. The two forms have appreciably differing absorptions for ultraviolet radiation. When a compound of this type is tested in the fluorimeter, difficulty is experienced in obtaining a reading immediately after insertion of the cells, as the galvanometer drifts continuously in one direction. If readings are taken at intervals of a few minutes, they are found to show a progressive change up to an hour or so, when a fairly constant reading is generally obtained, and this value is taken. We have met with one or two compounds, however, with which no steady state seemed to be reached and the test had to be abandoned. Whilst in position in the fluorimeter the cells are completely shielded from extraneous light, and as the change is slow, it is unaffected by the short irradiation with ultraviolet necessary to obtain a reading. The testing of a compound of this type is a slow process, as each solution has to be left in the instrument for an hour. Some saving in time might be made by carrying out the entire process in a darkroom with weak red illumination, but we have not tried this.

Strength Measurements on Substrates

Discussion of strength measurements on textile substrates will be mainly limited to the testing of chemically similar samples. The question of the comparative evaluation of chemically different products is much more difficult, and will only be touched upon in general terms. Here, again, there is a close parallelism with dyes. The strength determination of samples of the same dye is perfectly straightforward, whereas any attempt to determine the relative tinctorial values of dyes which are chemically different and of different colour is bound to be difficult: a range of answers will be obtained, depending on which other dyes are added to produce the same final colour, and also on the type of illumination. However, if these conditions are specified, a fairly accurate comparison can be given, because small colour differences can be judged easily by eye when they occur in colours of moderate depth.

Matters are rather worse, however, if an attempt is made to compare chemically different brightening agents which produce fluorescence of different colours. The precise tone of the "white" produced will depend upon the illumination— both its visible colour and its ultraviolet content— and upon the initial colour of the substrate. In addition, the accuracy of visual judgment is low, because the eye is dealing with "near whites". A change of 20% in the quantity of brightening agent applied makes little difference to the "white" produced. This is in sharp contrast, for instance, to a grey produced by a mixture of three dyes, in which a 2% change in concentration of any one dye is clearly visible.

VISUAL METHODS

The simplest method of comparing samples of the same product might seem to be the same as for determining a parity between dyes: a range of strengths of one is compared with one or more dyeings of the other, to find two which are equal. If this method is tried with fluorescent brightening agents, two of the three difficulties just mentioned in the case of chemically dissimilar products are present here also: firstly the quality of the "white" depends on the illumination, and secondly the eye is unable to compare "near whites" accurately. Our own experience has convinced us that accurate assessment cannot be made in daylight. Even if the illumination is standardised by using a colour-matching type of fluorescent lamp— which emits some ultraviolet— or a more complicated arrangement of tungsten and "black" lamps, very little improvement is obtained. Examination in daylight is, however, a necessary part of the evaluation of a sample, with particular regard to yellowness due to the compound itself or impurities, but only a rough estimate is possible.

The next obvious method is to compare the ranges in a darkroom, under ultraviolet illumination from a "black" lamp. Under these conditions, only the fluorescence is visible, so that the patterns appear bright blue or violet. This is a perfectly valid method of comparison, provided that one is dealing with chemically similar products, and it is certainly more accurate than judging "whites" in daylight. Ability to judge strength differences is, however, lower than when comparing ranges of dyeings in daylight, and it is probable that the eye is upset by the abnormal viewing conditions, in which bright areas of fluorescence are seen in surrounding darkness.

If this method of testing is adopted on cellulosic materials, it may be found that the patterns are too unlevel to permit comparison. This condition is likely to arise unless great care is taken in preparation. The properties of many of these compounds resemble those of the cold-dyeing

direct dyes such as Cotton Yellow CH. To obtain a uniform application, treatment should be carried out cold or at a moderate temperature, commencing without salt and adding 20–30% Glauber's salt after 10 min. or so. Adequate turning of the material is essential, or alternatively treatment with the material laid flat in a large shallow vessel. Total time of treatment may be 45–60 min., after which the materials are whizzed or squeezed without rinsing, and dried at room temperature, preferably stretched on a pin-frame. On no account must drying on a hot cylinder be resorted to, or migration is certain to occur, with consequent unlevelness.

It having been found that the accuracy of this method of estimation was mainly limited by the sensitivity of the eye, the next step was naturally to investigate the possibilities of a technique analogous to the "cross-dyeing" used in dye estimation. In this process differences in depth are converted into differences in colour by addition of a constant amount of a dye of another colour. For example, in estimating a yellow dye, a constant quantity of blue dye is added to each dyebath, and differences in depth of yellow are thereby converted to variation from blue–green to yellow–green, the eye being much more sensitive to the latter.

Since brightening agents produce a blue to violet fluorescence, if an orange–red fluorescence were added to this the result would be a magenta, varying from redder to bluer with increasing quantity of brightening agent, a variation which should be easily visible. The number of possible compounds was very limited, but for cellulosic materials Direct Safranine RW proved suitable. Its fluorescence was very weak compared with that of brightening agents, the maximum being at a strength of about 0·5%, when applied cold in the same manner as a fluorescent brightening agent. A strength of 0·5% was therefore standardised, but even so the concentration of brightening agent had to be very low, 0·001–0·01%, to give the desired effect. The application of such small quantities of brightening agent required great care in avoiding contamination, but when a satisfactory range had been obtained, it was found that concentration differences of 10% were clearly visible, and smaller differences could be estimated with fair confidence.

We have used this Direct Safranine RW test for several years, but recently, when the problem was considered further, it appeared that in theory better differentiation would be obtained by using a yellow "cross-fluorescence", converting strength variation of a brightening agent into a transition from a yellowish white to a bluish white. A suitable dye was Oxyphenine R, but to obtain adequate exhaustion of this it is necessary to dye at the boil with a considerable quantity of salt. This means that this dyeing must be carried out before the application of the brightening agent, but this is not a great disadvantage, as a large amount of cloth can be prepared, and used as required. A concentration of 0·5% is suitable.

Furthermore, this method lends itself to the testing of brightening agents in detergent products. Cloth previously dyed in Oxyphenine R is simply washed in a suitable concentration of the detergent, under the desired conditions, and the resulting fluorescence is assessed as in a normal application of brightening agent.

For estimation on wool a suitable dye was found to be Quinoline Yellow in 0·25% concentration; this gives a bright yellow fluorescence and may be satisfactorily applied under the same conditions as a product such as Uvitex WS, viz. from a 5% formic acid bath at 60°C. Alternatively, of course, for estimation of brightening agents in detergents, the wool may be predyed with Quinoline Yellow, and then washed in the detergent; some bleeding generally occurs, but does not invalidate the method.

INSTRUMENTAL METHODS

A full spectrophotometer is generally ruled out on economic grounds, but for simple strength comparisons a more elementary instrument can be used. Unfortunately, there is no such instrument on the market, and anyone requiring one has to construct it himself. The design will, therefore, be described only in general terms, apart from a modification of the Hilger fluorimeter which we have found useful.

The light source has to be a mercury discharge lamp, as it is not really practicable to over-run a filament lamp sufficiently to obtain a useful amount of ultraviolet radiation. Unfortunately, some of the "black lamps" on the market do not have a steady arc. A "balanced" type of instrument is a virtual necessity, in which two photocells are used to give zero galvanometer deflection, but the normal form of this, in which two beams of light are taken from the lamp, is of no use with a wandering arc, and a beam-splitting prism becomes necessary. However, the lamp used in the Hilger fluorimeter—a Sieray 67 MB/D—appears to have a perfectly steady arc, and this instrument shows no signs of unsteadiness due to arc wandering.

Textile materials possessing a pronounced surface structure do not reflect equally in all directions, so it is necessary to use an "integrating sphere" to collect the fluorescent light emitted by the pattern. On account of possible unlevelness, it is advisable to measure a large area of material. The methods of doing this, in order of preference, are—

(*a*) Illuminate a large area
(*b*) Scan the pattern mechanically, illuminating a small area
(*c*) Make several measurements, illuminating a small area.

As the diameter of the integrating sphere requires to be, say, ten times the diameter of the illuminated area of pattern, methods (*b*) and (*c*) permit the use of a smaller integrating sphere, which may be an important constructional consideration.

The integrating sphere may be dispensed with if the pattern is always placed at the same orientation relative to the ultraviolet beam and the photocell,

or an average is taken of several orientations, but this is not a very satisfactory procedure.

Modification of the Spekker Fluorimeter

It occurred to us some years ago that it might be practicable to use the Hilger fluorimeter for reflection measurements, by constructing holders carrying a pattern at 45° to fit in place of the solution-cells (Fig. 4). In view of the foregoing remarks, such an arrangement is far from ideal, the illuminated area being only about 1 in. × ¼ in., and there being no provision for integrating the light. For the latter reason, we limited use of the instrument on cellulosic material to filter paper (Whatman No. 541), which had no surface structure. This paper, being hardened, is quite robust when wet. For protein material, wool felt should be quite satisfactory, but we have not tried this. The smallness of the illuminated area was overcome by averaging five pieces.

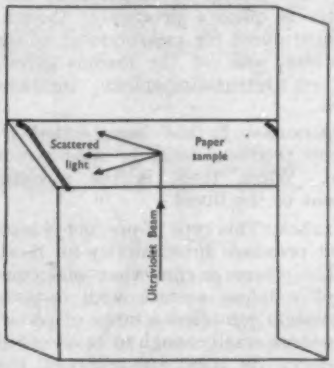


FIG. 4

The use of the instrument was exactly analogous to its use with solutions, the instrument being first balanced with the test piece, and the diaphragm fully open. The test piece was then replaced by an arbitrary stronger standard, and the diaphragm closed until balance was again obtained. The result was therefore obtained as a percentage of an arbitrary standard, and since only comparative results are generally required, this is sufficient. This simple adaptation of the fluorimeter has been found to work quite satisfactorily, though the large number of measurements make it rather tedious to use.

As an example of the results obtained, a range of concentrations of Uvitex RS were measured (Fig. 5–7). The percentage exhaustion of the solutions was determined on the fluorimeter by measurement of the original and exhaust baths, and is seen from the graph (Fig. 5) to fall from about 80% at very low concentration to about 25% at a nominal 5% application. From these data the nominal percentage applications were corrected to actual concentrations on the filter paper. The reflection of the latter was measured by the method just described, and a graph of reflection against actual concentration thus obtained (Fig. 7). This is seen to be a smooth curve of approximately

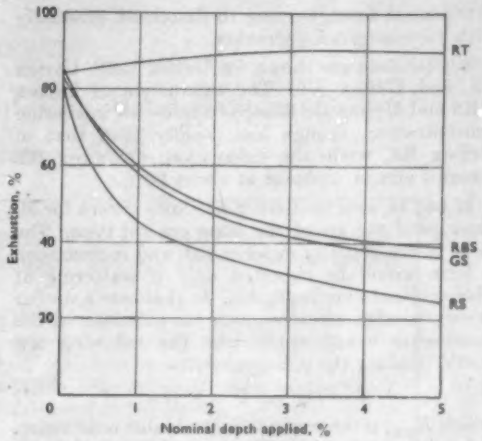


FIG. 5—Exhaustion of Various Uvitex Brands—Filter-paper (Whatman 541) at 20°C.; 50 : 1 liquor containing 5 g. Glauber's salt per litre for 1 hr.

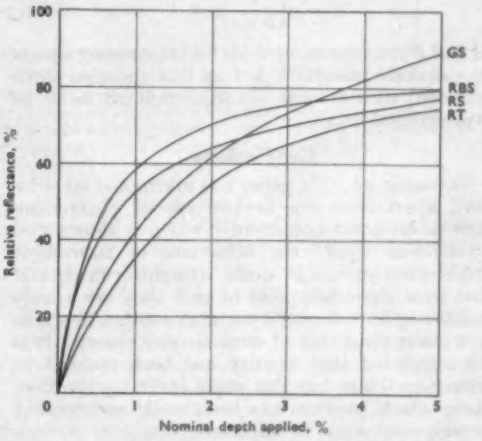


FIG. 6—Relative Reflectance Values for Various Uvitex Brands on Filter-paper (Whatman 541)—50 : 1 liquor containing 5 g. Glauber's salt per litre for 1 hr. at 20°C.

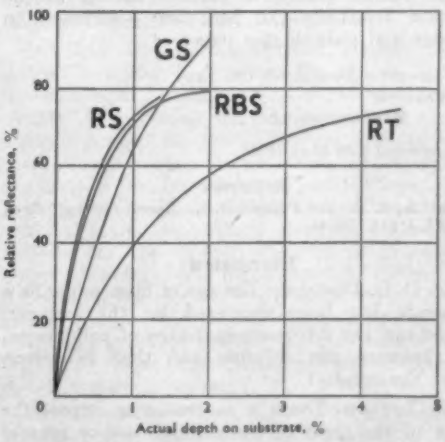


FIG. 7—Relative Reflectance Values for Various Uvitex Brands on Filter-paper (Whatman 541)—50 : 1 liquor containing 5 g. Glauber's salt per litre for 1 hr. at 20°C.

exponential form, tending to flatten off gradually with increasing concentration.

Similar data are shown for Uvitex RBS, Uvitex GS, and Uvitex RT. The exhaustion of Uvitex RBS and Uvitex GS is seen to fall with increasing concentration, though less rapidly than that of Uvitex RS, while the exhaustion of Uvitex RT remains almost constant at about 90%.

It will be seen that the reflectance curves for all three products are of the same general type. The form is not actually exponential, and in fact such a form would be expected only if scattering at fibre surfaces were negligible. In that case a similar theory to that already given for solutions in the fluorimeter would apply, and the following law would hold for the reflectance R—

$$R = R_{max}\,(1 - e^{-ac})$$

where R_{max} is the maximum attainable reflectance. It has been claimed by Glarum and Penner[1] that a more complicated relation, the Merritt law—

$$R = A\left(\frac{c}{B + c}\right)e^{-ac}$$

(A and B are constants) holds for brightening agents on cellulosic materials, but as this contains three unknown constants, it is rather difficult to fit to experimental results.

Conclusions

Summing up, this paper has attempted to show that, apart from one or two special phenomena such as *cis–trans* isomerism— which is shown also by stilbene dyes— the behaviour of fluorescent brightening agents is quite straightforward, and that from the user's point of view they are merely another special class of dyes, whose estimation is in fact easier than that of certain other classes. It is not suggested that finality has been reached in testing methods, but this paper indicates the lines along which progress has been made and further development may be expected.

* * *

The author wishes to express thanks to the Clayton Dyestuffs Co. Ltd. for permission to prepare and publish this paper.

THE CLAYTON DYESTUFFS CO. LTD.
CLAYTON
MANCHESTER 11

(*MS. received 12th May 1955*)

Reference

[1] Glarum, S. N., and Penner, S. E., *Amer. Dyestuff Rep.*, **43**, P 310 (1954).

Discussion

Mr. D. O. DOUGLAS: The use of filter paper as a substrate has been suggested by the lecturer. Would not the difference in degree of polymerisation between the cellulose and that in cotton affect the results?

Mr. TAYLOR: There is no reason to expect the effect of the state of the cellulose to be greater than with, say, a direct cotton dye. While there might be small quantitative differences in exhaustion, the object of the filter-paper experiments was to give a general picture of the behaviour of a few fluorescent brightening agents.

Mr. DOUGLAS: Has the lecturer any knowledge of the method recently suggested by the British Launderers Research Association?

Mr. TAYLOR: We have not yet had any experience of the B.L.R.A. method.

Mr. L. TELESZ: Is it possible to adapt the methods outlined by the lecturer to assess fastness properties to light and washing?

Mr. TAYLOR: Only the instrumental method of fluorescence measurement is suitable, as obviously in the "cross-fluorescence" method the light-fading behaviour of the brightening agent will not be normal in the presence of another dye. The cross-fluorescence method should be quite satisfactory, however, for assessing wash-fastness, though we have not actually used it for this purpose. Our simple modification of the Hilger fluorimeter is quite a practicable though rather tedious instrument for measurement of light and wash-fastness, and for the reasons given in the lecture an integrating-sphere instrument is preferable.

Mr. DOUGLAS: It has been stated that the fluorescent products used in wash-powders are insoluble. What, then, is the mechanism of attachment to the fibre?

Mr. TAYLOR: This type of product is insoluble in water but possesses substantivity for most textile fibres. The process is somewhat analogous to the dyeing of cellulose acetate with disperse dyes. The suspension comprises a range of particle sizes, including those small enough to be adsorbed on the fibre surface. As these are removed, the larger particles gradually break down.

Mr. C. A. MILLS: In the matching of works batches of fluorescent-tinted whites, would examination under an ultraviolet lamp ensure greater accuracy than daylight?

Mr. TAYLOR: Considerably greater accuracy would be obtained by the use of a "black" ultraviolet lamp and a standard sample for comparison. If very high uniformity were desired, the fluorescence could be measured by means of a simple photocell and a galvanometer.

Mr. A. G. TYLER: Use of spectrophotometers has been mentioned. Would there be any advantage in using a light source of wavelength, say, 300–400 mμ.?

Mr. TAYLOR: Measurement over a continuous wavelength range, as suggested, has certainly at least a theoretical advantage over use of a mercury lamp, with only one wavelength of 367 mμ., as conditions are then nearer to those of sunlight. The methods of assessment in the paper were, however, specifically limited to chemically identical products— for other reasons besides absorption characteristics— and for these, measurement at a single wavelength is, of course, quite adequate. A continuous waveband would be practically essential if any attempt were made to compare chemically different products.

COMMUNICATION

The Irgalan Dyes—Neutral-dyeing Metal-complex Dyes

GUIDO SCHETTY

Dedicated to the late F. L. Goodall, M.Sc., F.R.I.C., F.S.D.C., Joint Managing Director of The Geigy Company Ltd., Manchester, who was President of the Society of Dyers and Colourists during 1953–1954.

Mr. Goodall took a very keen interest in the field of neutral-dyeing metal-complex dyes, which have recently become very popular, and he enriched and enlarged this field by his own dyeing experiments and ideas. His was the special merit of recognising for the first time the particularly favourable behaviour of Irgalan dyes, which, from the application point of view, is fundamentally different from that of the metal-free milling dyes.

As one of the initiators of the present work, he helped with the drafting of this paper in the spring of 1954. Unfortunately, owing to his very sudden and early death, he did not live to see the completion of this paper.

The chemistry of chromium-complex dyes is discussed in relation to dyeing properties on wool, with particular reference to the problem of avoiding skittery dyeing arising from differences between individual wool fibres. The structural features required for dyes to give non-skittery dyeings under neutral conditions are deduced, and it is shown how these researches resulted in the production of the Irgalan (Gy) dyes.

INTRODUCTION

In 1949 a new type of metal-containing dye was put on the market by J. R. Geigy AG. of Basle under the name of Polar Grey BL (later renamed Irgalan Grey BL). This dye was recommended for the fast dyeing of wool from a neutral or weakly acid bath. By this step a novel dyeing idea, pursued for several years, was put to a practical test.

When Polar Grey BL had successfully passed its period of testing, other dyes of this type were put on the market and in 1951 were grouped together under the name Irgalan dyes, a series of dyes having closely similar behaviour in dyeing. Meanwhile (1950) E. I. du Pont de Nemours & Co. Inc. introduced a chemically similar range under the name Neutracyl dyes (since 1951 termed Capracyl dyes). These colouring matters were recommended for the dyeing of nylon. Further ranges of dyes with similar chemical and dyeing characteristics then appeared in rapid succession. In order of appearance these were the Vialon Fast dyes (BASF 1951), recommended for the dyeing of synthetic polyamide fibres such as nylon and Perlon, the Cibalan dyes (Ciba 1952), the Lanasyn dyes (S 1952), the Supralan dyes (G 1953), the Isolan dyes (FBy 1954), the Pharmetal dyes (now named Neutralan dyes, Pharma Chemical Corpn., New York, 1954), and the Ortolan dyes (BASF 1954).

All these dye ranges consist of chromium- or cobalt-containing azo dyes, containing no ionising lyophilic groups, in which two dye molecules are combined with one metal atom (2 : 1 complexes).

H. D. K. Drew and R. E. Fairbairn [1] first published the constitution of such complexes. However, being insufficiently water-soluble, these complexes were not textile dyes.

In 1941 J. R. Geigy [2] published the observation that certain novel water-soluble salts of chromium compounds derived from *oo'*-dihydroxyazo dyes containing no sulphonic acid groups give level dyeings on animal fibres from a weakly acid bath. This German patent [2] was a considerably condensed version of a much broader patent application in Germany dated 31st December 1938, which was withdrawn owing to insufficient proof of technical superiority of one of the claimed compounds in relation to previously known products.

In 1941 IG. Farbenindustrie applied for a patent covering a "process for dyeing animal fibres, also in admixture with vegetable fibres or leather" [3], in which the dyeing of the animal fibres is carried out from a neutral bath, in some cases with previously known metal-complex colouring matters free from sulphonic acid groups. This process was published after the claimants had already found that such complex types were suitable for the dyeing of synthetic superpolyamide fibres [4] and had made provision for marketing such dyes under the brand name Perlon Fast [5]. Lastly, also in 1941, du Pont applied for a patent [6] covering a process by which superpolyamide fibres are dyed from dispersions of water-insoluble, metal-containing dyes.

This situation shows how different research laboratories, working simultaneously and independently, investigated similar types of dyes, in some cases for entirely different reasons.

The present paper gives a comprehensive picture of these novel groups of dyes and attempts not only to describe their dyeing behaviour but also to explain this in relation to their chemical background. In this we will discuss our own development work, and it will become apparent how this led to the Irgalan dyes. Publications concerning analogous dye classes have already been made by other authors [7].

HISTORICAL BACKGROUND

The fact that treatments with metal salts improve the fastness of textile dyeings has been known for a considerable time, and has always stimulated the dyer to employ new methods in order to improve his work [8]. In the past century chromium salts have come more and more into prominence amongst other metal salts as a means of improving fastness. Nietzki's discovery [9] of synthetic lake-forming dyes, i.e. dyes which react with metal salts, initiated the development of the true chrome dyes. The great improvement of fastness obtainable with such dyes gave tremendous impetus to chemists of those days not only to increase the range of the available chrome dyes but also to clarify and gain an understanding of the chemical reactions underlying the metallisation of the dyes. Meanwhile dyers evolved practical processes for their bulk application. At the turn of the century, therefore, fundamental inventions and discoveries were made in the field of the fast dyeing of wool, among which a few of outstanding importance were the metallising capacity of the *oo'*-dihydroxyazo dyes, the invention of the one-bath chrome process (metachrome dyeing process), and Werner's coordination rule, which was expanded by P. Pfeiffer and his school to apply to organic complex-forming compounds.

In 1912 the Badische Anilin- und Soda-Fabrik applied for a patent covering a process discovered by René Bohn and consisting in treatment of hydroxyanthraquinonesulphonic acids and their derivatives with warm solutions of chromic salts [10]. The basic idea behind this patent was to combine the metal in substance with mordant dyes usually fixed on wool as chromium lakes in a two-bath process, so that the dye–chromium complex could be applied to wool by a single-bath method. Such dyeings were supposed to have the high fastness of the mordant dyes themselves. However, the dye complexes cited in the patent had very little affinity for wool. Being found unsuitable for the dyeing of wool, they were suggested for the colouring of inks and later also for the production of fast prints. In the same year chromium complexes of mordant dyes of the azo series were also made the subject of a BASF patent application [11]. However, all these inventions had no practical application as yet. In 1915 the Society for Chemical Industry in Basle (now Ciba) applied for a patent [12] for the fundamental invention according to which animal fibres are dyed with chromium-complex dyes from acid baths preferably containing mineral acid. The patent [13] covering this invention proposed in particular dyeing from a strong sulphuric acid bath and forms the basis of the Neolan (Ciba) and Palatine Fast (BASF) dyes marketed in 1919. In the last thirty years these dyes have undergone great development, and today they occupy an important place amongst wool dyes and are also marketed by other firms under different names. All these dyes have a similar chemical constitution, i.e. they are azo dyes containing sulphonic acid groups and a single co-ordinated chromium atom per molecule of dye (1 : 1 complexes).

ORIGIN AND SOLUTION OF THE PROBLEM

When, in the middle thirties, Geigy decided to explore the field of metal-complex dyes for wool, there appeared to be little possibility of improving the excellent products already on the market, and this field, covered as it was by over two hundred German patents, appeared to have been completely explored. In order to conduct research with any hope of success, it would therefore be necessary to find metal-complex dyes with novel dyeing properties. Since the known chromium-containing dyes required application from a strongly acid dyebath, it appeared desirable to look for dyes which could be applied under less strongly acid conditions and yet would retain the desirable properties of the chromium-complex dyes which were known at that time.

In order to achieve this object, an entirely different route would have to be taken at the outset from that leading to the strongly acid-dyeing metal-complex dyes. Instead of asking how chromium-containing dyes could be dyed on wool, we had to ask what should be the constitution of metal-complex dyes in order to yield practically useful wool dyeings under specified conditions of application. In this approach, research was bound to encounter types of compounds already protected by comprehensive patents. Therefore the new idea could succeed only if, in addition to the discovery of a suitable but already known type of compound, a patentable invention was made.

A major difficulty was the fact that chromium-complex dyes free from sulphonic acid groups but containing sulphamyl ($-SO_2 \cdot NH_2$) solubilising groups had been patented [14], though apparently the applicant had not recognised the significance thereof, probably because the compounds offered for patent protection dye wool raw stock skittery and uneven from a neutral dyebath [15], and therefore belong rather to the class of chromium-complex dyes requiring strongly acid dyeing conditions. The chromium complex of —

2-Amino-1-hydroxyphenyl-4-sulphanilide→β-naphthol

which is suitable for the dyeing of wool under very mild conditions, had been mentioned nine years earlier, but was not recognised as such by the patentee [16]. Of the chromium-complex dyes free from sulphonic acid groups but containing sulphamyl groups, both those with substituted and those with unsubstituted nitrogen were already known.

Geigy eventually discovered methylsulphonyl-substituted complex dyes free from sulphonic acid groups, a type of dye particularly suitable

for the dyeing of wool under conditions giving the best fibre preservation [18]. This discovery was the result of special studies relating the phenomenon of levelling in wool dyeing to the constitution of the colouring matter applied. The discussion of Irgalan dyes is therefore preceded by separate sections dealing with problems of levelling and their relation to the chemical constitution of dyes for wool.

LEVELLING POWER OF WOOL DYES

Levelling results from several simultaneous processes [19]. The following characteristic defects of wool dyeings are known—spotty or cloudy dyeing, poor penetration, and skitteriness. Bad penetration and spottiness can both be remedied by suitable dyeing methods, e.g. the regulation of liquor circulation, hydrogen ion concentration, and temperature. These principles have been discussed in detail elsewhere. However, skitteriness is a specific property of a dye and is of considerable importance for the solution of our problem. The definition of wool dyed skittery is that the dyeing intensity varies within the smallest semi-microscopic areas. Unlevel wool of this nature resembles in its appearance the surface of a statistically homogeneous mixture of light, medium, and dark grains of sand. Judging the degree of unlevelness with the naked eye is difficult, and is strongly influenced by subjective factors in the observer. A safer method of judging skitteriness is observation of thin microscopic cross-sections of densely packed fibre bundles (see Fig. 1 and 2).

Skitteriness comes about through selective dyeing of different wool fibres. Skittery-dyed wool can therefore be described as that in which individual fibres show big differences in depth of dyeing. Wool textiles may of necessity consist of very different fibre qualities. In wool fibres of different origin and even within a single wool fibre there are morphological and chemical differences that need not be discussed in the present paper. A dye not giving rise to skittery dyeings covers such differences, and in an ideal case will dye equally rapidly on all fibres present regardless of differences in wool quality. A dye which is selective, i.e. skittery, in dyeing behaviour, however, will show marked differences in the rate of exhaustion (Table I).

TABLE I

Time of Half Dyeing ($t_{\frac{1}{2}}$) of Polar Red RL
(pH 3·3; liquor ratio 100 : 1)

Wool Quality	$t_{\frac{1}{2}}$ (min.)
Low-grade slubbing ...	14·5
Tippy wool	24·3

It is important not to confuse skitteriness (fibre unlevelness) with the uneven appearance caused by the fact that a poorly migrating dye shows differences in depth when dyeing the threads of very densely woven textile materials. Subsequent displacement of the weft and warp threads bares these places, and a surface irregularity is thus shown which may be regarded as skittery but is due entirely to poor penetration.

RELATION BETWEEN CHEMICAL CONSTITUTION, NON-SELECTIVE DYEING BEHAVIOUR, AND ACID REQUIREMENT OF A WOOL DYE

There are, in principle, three ways of obtaining a level dyeing on wool—

(1) To minimise, or remove, differences existing in the wool by modification of the fibre.

(2) To modify the dyeing conditions in such a way that variations in depth due to differences in the wool are avoided.

(3) To apply dyes which do not accentuate chemical differences within a chemically undamaged mixture of different wool qualities or grades.

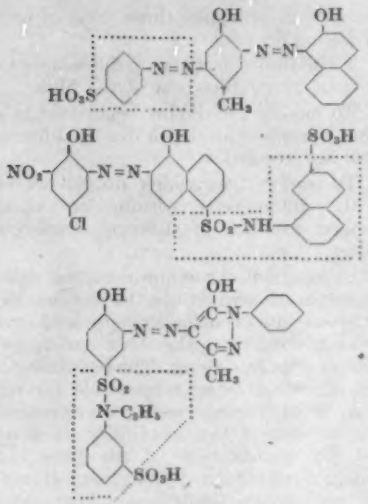
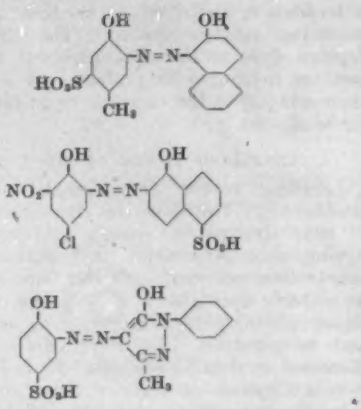
In the case of chromium-complex dyes containing sulphonic acid groups the problem has been solved by method (2) using strongly acid dyebaths. Under such conditions the wool undergoes some modification during dyeing. The possibility of such fibre modification being responsible for ultimate levelness is at present under investigation. In tests to determine the suitability of a dye for method (3) modification of the fibre must be reduced to a minimum. Dyeing must therefore be carried out under conditions giving maximum protection to the fibre, i.e. preferably within the isoelectric range of wool.

These conditions require the dye to have a sufficiently high rate of exhaustion within the desired ranges of acidity. We have been able to show that a high rate of dyeing on chemically undamaged wool goes to a great extent hand-in-hand with non-selective dyeing character.

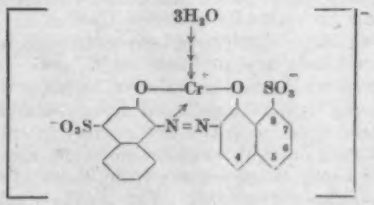
According to a working rule employed in dye synthesis, increased molecular size raises the exhaustion of a dye on wool. It appeared possible at first glance to increase the non-selective affinity of the already known chromium-containing dye types by increasing their molecular weight. From the point of view of preparation of such dyes there are many possibilities, such as enlarging the molecule by synthesis of disazo dyes or by incorporating larger nuclear substituents such as e.g. aryl sulphones, arylsulphonic esters, aryl ketones. We have synthesised a series of such chromium-containing dyes with enlarged molecules and have compared them with the dye nearest in chemical constitution but with a smaller molecule. Examples of such comparisons are shown in Table II as the non-metallised dye acids. The groups increasing the molecular size are shown enclosed by dotted lines.

The majority of such dyes with increased molecular bulk have better exhaustion than the corresponding smaller ones. However, not only is the non-selective dyeing character not improved, but actually it is somewhat decreased by this method. Especially from strongly acid dyebaths they tend to dye more skittery than the comparable products of smaller molecular size. The larger dye molecules tend to dye preferentially the tip of the wool fibre. Their higher affinity prevents migration towards the root of the wool fibre in a strong sulphuric acid dyebath in spite of the loosened root structure of such fibres.

TABLE II

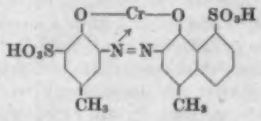
Dye with Increased Molecular Size	Smaller Form for Comparison
	

Experiments by Ender and Müller [20] show that the exhaustion of chromium-complex dyes depends on their ionic charge. Monobasic dye acids dye better than zwitterionic complexes, whose total external charge is zero. Amongst all dyes tested, Palatine Fast Blue GGN is particularly noticeable with its comparatively steep exhaustion graph. Amongst the entire group of Palatine Fast dyes it shows the highest levelling power. This results in a solid and non-skittery dyeing by the strong sulphuric acid method. Palatine Fast Blue GGN is the 1 : 1 chromium complex of a disulphonated acid dye; according to Formula (I) it is the colour salt of a monobasic acid.



(I)

Isomeric complexes in which the sulphonic acid group occupying the *peri* position to the metallisable hydroxyl group has been moved into the position 7, 6, 5, or 4 show different behaviour in dyeing. They show poor levelling and exhaustion in strong sulphuric acid baths and furthermore have a more reddish tone. However, they are faster to alkali. These differences emphasise the peculiar importance of the sulphonic acid group in the *peri* (8) position. In order to understand the connection between the constitution and non-selective dyeing character, it was extremely important to recognise that by chelation of the sulphonic acid with the hydroxyl groups, which is possible in the *peri* position, greatly reduced hydrophilic character is obtained [21]. If in Formula (I) above the sulphonic acid group in the *para* position to the azo group is replaced by a sulphonic acid group capable of chelation, a dye with even better levelling and exhausting powers is obtained. The chromium-containing dye II [22] yields even with a bath containing only 3–4% formic acid completely level wool dyeings with good exhaustion.



(II)

Reduced hydrophilic character has thus not only reduced the acid requirements in dyeing but has also improved the non-selective dyeing properties. The question now arises how the hydrophilic character of a compound of type II could be reduced further and whether by such modification weakly acid or even neutral dyeing chromium-complex dyes with completely non-selective dyeing properties could be obtained.

Which are the hydrophilic centres in compound II? As in Palatine Fast Blue GGN (I), the hydrophilic centres are the sulphonic acid groups, the normal solubilisers, which, as explained above, may be made to lose a portion of their hydrating power by suitable positioning within the molecule.

The solubilising action of a sulphonic acid group depends on the property of its anions of forming co-ordinate linkages with water according to formula III.

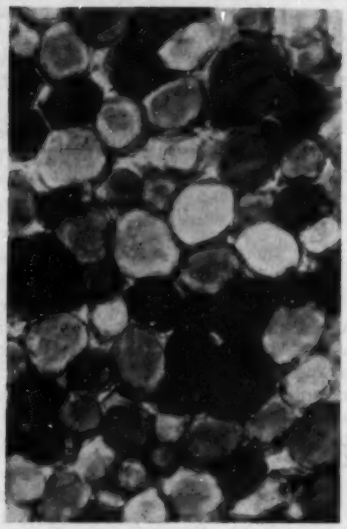


FIG. 1—Fibre Cross-section of Skittery Dyeing

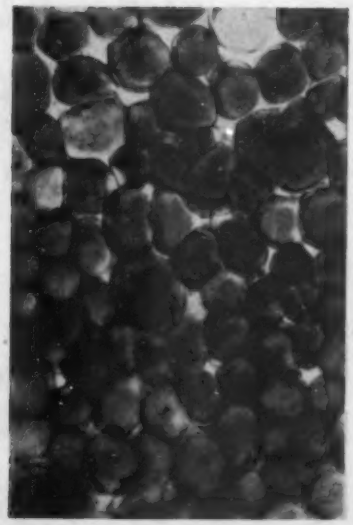
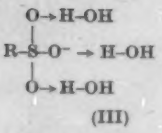


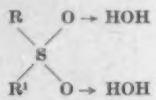
FIG. 2—Fibre Cross-section of Level Dyeing

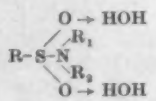


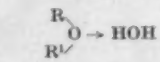
(III)

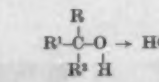
The oxygen atoms of the sulphonic acid group, acting as electron donors, associate with hydrogen atoms of water and thus impart water solubility. If this kind of action of sulphonic acid groups is generalised, it may be assumed that all strong electron donors should have more or less hydrophilic character. In principle, such strong electron donors may be oxygen, sulphur, and nitrogen atoms and in certain cases even carbon atoms as long as these atoms are present in suitable linkages, i.e. where they are able to display basic properties. The following examples may be mentioned in particular—

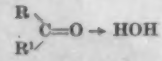
OXYGEN ATOMS IN—

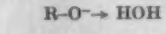
Sulphones 

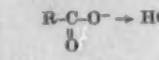
Sulphonamides 

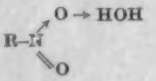
Ethers 

Alcohols 

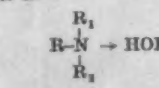
Ketones 

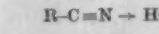
Hydroxyl ions 

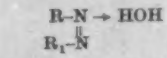
Carboxyl ions 

Nitro groups 

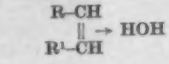
NITROGEN ATOMS IN—

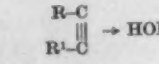
Amines 

Nitriles 

Azo groups 

CARBON ATOMS IN—

Alkenes 

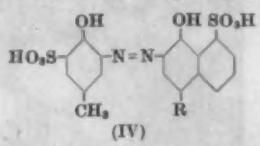
Alkynes 

SULPHUR ATOM IN—

Thioethers

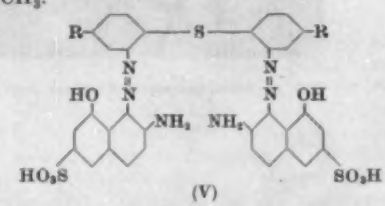
To illustrate the tinctorial properties of the groups listed above, a few typical examples may serve. In the 1 : 1 chromium complexes of Formula (IV) a decreasing rate of exhaustion can be noted when the radical R is varied according to the following series—

$R = -CH_3, -CO\cdot CH_3, -CHO, -CH_2OH$



(IV)

Experiments in the field of metal-free acid dyes have shown that the same rule holds true— strong electron donors reduce the neutral exhaustion and increase the tendency to skittery dyeing. For example, the γ acid dye (V) has better exhausting power when R = H and smaller tendency towards skittery dyeing than when $R = SO_2\cdot CH_3$ or $CO\cdot CH_3$.



(V)

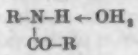
The reduction in exhausting power by entry of a further sulphonic acid group into the already sulphonated acid wool dyes is now universally known, so that a further discussion of this phenomenon may be omitted, although it is a very good illustration of our deductions.

All these properties, however, are not sufficient to explain the tinctorial behaviour of 1 : 1 chromium complexes containing sulphonic acid groups and do not enable us to bridge the gap between them and the metal-free acid wool dyes. The question of explaining the main differences existing between chromium-containing and metal-free dyes with otherwise equal electrical charge still remains unanswered. Ender and Müller [23] have shown that the Palatine Fast dyes are linked to the wool substance not only by the sulphonic acid groups (electrovalency) but also by means of the chromium atom (co-ordination). The strongly acid dyeing chromium-complex dyes would therefore appear to occupy a special place. However, this is not the case if the chromium atom in the 1 : 1 chromium-complex dyes containing sulphonic acid groups is regarded as another very active centre of hydration. In contrast to the hydrophilic groupings mentioned, the chromium atom functions as an electron acceptor; i.e. the linkage chromium–water takes place via the lone electron pair of the oxygen atom in water (VI).

(VI)

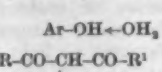
Substituting for the term "co-ordinating chromium atom" the general term "electron acceptor" enables us to make a comparison with acid wool dyes. When considering the elements present in dyes (metals, carbon, hydrogen, nitrogen, oxygen, and sulphur) it is not difficult to recognise that apart from metals only hydrogen can act as the electron acceptor. In each individual case it has to be shown whether hydrogen atoms capable of covalency are present. It may be assumed that all the mobile acidified hydrogen atoms show a co-ordination number of 2, i.e. they are capable of forming hydrogen bonds. For example, in the following groupings hydrogen is capable of such bonding and is thus able to hydrate —

Carboxyamides and acylamino groups

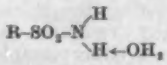


Hydroxyaryl groups $Ar–OH \leftarrow OH_2$

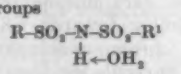
1:3-Diketones



Sulphonamide groups



Disulphonimide groups



When comparing chromium with hydrogen the high coordination number of 6 compared with 2 of hydrogen is important. The two hydrogen bonds are not as stable as the six chromium ones. Furthermore, there are great differences in charge between these two elements. In this way such considerable differences between the two atoms result that up to now the fundamentally similar mode of action of external hydrogen bonding in dyes has been overlooked.

The following examples illustrate how in metal-free acid wool dyes the rate of exhaustion is not only reduced by increasing the externally bonding hydrogen atoms but the tendency to dye skittery is also increased (Table III).

Before proceeding further the above results are summarised as follows—

(1) Lower exhausting power and skittery dyeing go hand-in-hand

(2) Poor exhaustion and skittery dyeing are caused by too highly hydrophilic character of a dye

(3) Hydrophilic character is brought about not only by the action of electron donors but also by electron acceptors.

The following conditions are necessary for the constitution of a chromium-complex dye giving good exhaustion and non-skittery dyeings—

(*a*) The complex should carry a negative charge

(*b*) Any residual valency of metal atoms to be nearly completely or completely saturated

(*c*) The solubilising groups to be as little hydrophilic as possible

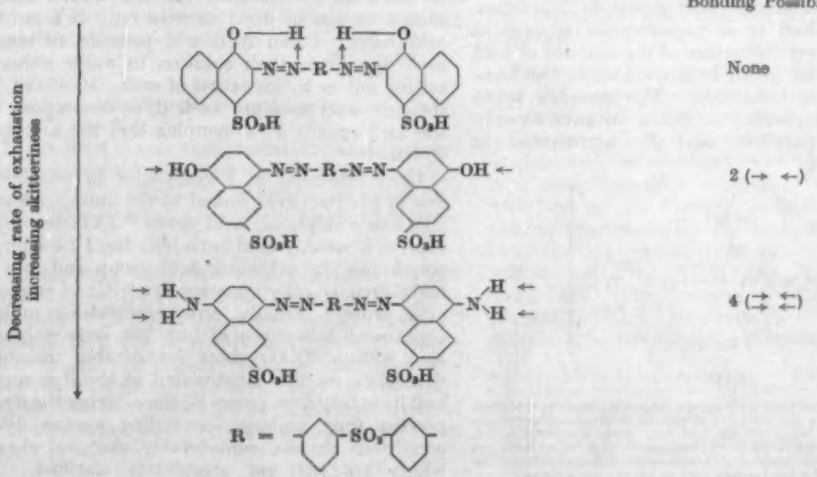
(*d*) The complex molecule to contain none or as few hydrophilic groups as possible.

An additional requirement as shown in the section entitled "Irgalan Standard" is that the individual members of a dye range should have equal exhausting power.

The dyeing properties are discussed below of a few complex types which were synthesised with the aim of meeting points (*a*)–(*d*) in the above working theory.

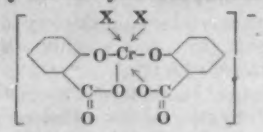
B. Eistert [24] mentions that co-ordination of ammonia to the chromium atom of Palatine Fast dye types yields ammine complexes which behave like normal acid wool dyes. We could not

TABLE III



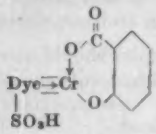
confirm these observations in the dyes investigated by us, as apparently the valency positions blocked by ammonia became freed during the dyeing process.

By chroming azo dyes containing sulphonic acid groups [25] with salicylatochromiates of general formula VII, 1 : 1 chromium complexes are formed in which two valencies of the chromium atoms are occupied by the salicylic acid residue (VIII).



$X = H_2O, NH_3, \frac{1}{2}(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)$

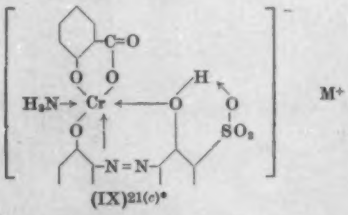
(VII)



(VIII)

Such dyes have similar behaviour to the already known 1 : 1 chromium-complex dyes containing no salicylic acid. Presumably the loss of hydrophilic character (due to saturation of two co-ordinate valencies) is compensated by the addition of two negative charges, or, during the dyeing process the salicylic acid is either completely or partly split off again, since it could be established that such complex types show little stability towards acids. Heating the dye solution with acid for a short time splits off salicylic acid quantitatively [21(e)]. The 5-sulphosalicylic acid gives a more stable linkage, but dyes containing instead of salicylic acid as in Formula VIII sulphosalicylic acid showed no improvement in dyeing properties in the desired sense, evidently because of addition of a further hydrophilic group.

Attempts to reduce the hydrophilic character of the sulphonic acid group by synthesis of dyes containing a sulphonic acid group in "chelation position" resulted in a considerable increase of exhausting power (reduction of the amount of acid required) as well as an improvement in the non-selective dyeing behaviour. The complex types tested, the composition of which we have already published in part [21(e)], may be represented in principle by IX.



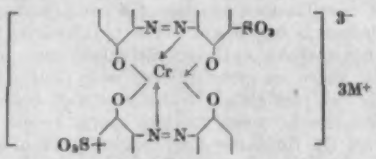
(IX)[21(e)]*

* The assumption that hydroxyl hydrogen atoms in *ortho* or *peri* position are not split off by metallisation as protons is supported especially by the high pK value of the hydroxyl group in 1:8-naphthol-sulphonic acid (pK = 12·6) in comparison with the hydroxyl groups in non-chelate position of the isomeric naphtholsulphonic acids. pK values of 8·2 for the 1:4-acid vary to 9·3 (for the 2:8-acid) [26].

From the standpoint of structure such chromium-containing dyes fulfil* all conditions desired for the constitution of an acid wool dye—anion-active character and all-round decrease in hydrophilic nature are achieved by masking of the chromium valencies and placing of sulphonic acid groups in chelate position. Comprehensive synthetic and dyeing investigations have shown, however, that this group of dyes can only approach the desired aim up to a certain degree and not in an entirely satisfactory manner. It is true that with regard to acid requirements such dyes differ quite considerably from the sulphonic acid group containing chromium-complex dyes now on the market. Even with 3–4% formic acid completely satisfactory wool dyeings are obtained. The acid requirement differs, however, only in degree from that of the classic chromium-complex dye and the chelation of the sulphonic acid group results in a series of undesirable dyeing disadvantages, the most important being the relatively low fastness to light.

On the fibre the chromium can be shown to be present by topping with chromable dyes [23], an indication that during the dyeing process the linkages saturating residual valency of the chromium atom are either completely or partly loosened. These very unsymmetrical complexes have little stability towards acid.

Sulphonated chromium-complex dyes which contain per dye molecule less than one metal atom have been mentioned in the literature [27] (X).

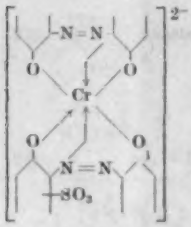


(X)

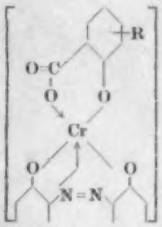
The coordinate valencies of the chromium atom are saturated. However, the hydrophilic character is increased by the two sulphonic acid groups to such an extent that for the above reasons such dyes can be dyed on wool only in a strongly acid bath. Often it is not possible to recover such dyes from their solution in water either by salting out or by an excess of acid. However, in a strongly acid medium such dyes decompose into the zwitterionic 1 : 1 complex and the metal-free dye acid.

Unsymmetrical 2 : 1 complexes in which only one of the two dyes linked to the chromium atom contains a sulphonic acid group [28] (XI) decompose even in a weakly acid bath into the 1 : 1 complex containing the sulphonic acid group and into the metal-free *oo'*-dihydroxyazo dye without sulphonic acid group. Finally, unsymmetrical complexes containing salicylic acid but free from sulphonic acid groups (XII) show undesirable instability depending on the constitution of the dye residue and its substituent group R, since during the dyeing process they undergo, according to the dyeing conditions chosen, considerable chemical changes which are not yet completely clarified. The

dyeing and chemical properties of wool dyed with them permit such possibilities as disproportionation into a 2 : 1 complex as well as formation of a coordinatively unsaturated 1 : 1 complex, the salicylic acid residue being split off. Pyrazolone dyes are most stable and show a pronounced tendency towards formation of 1 : 1 chromium complexes.



(XI)



R = H or non-ionic substituent

(XII)

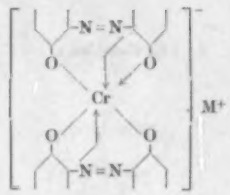
For reasons shown Geigy have abandoned this type, the preparation of which by means of salicylatochromiates was patented in Germany [2]. The aim of masking 1 : 1 complexes not containing sulphonic acid groups with colourless ring-forming complex-formers has now been realised with the Neopalatine (BASF) dyes [29], which appeared on the market in 1954 after a new method for their preparation had been patented (Pfitzner [7]). Although all the chromium-complex dyes discussed above more or less fulfil the desired requirements listed on p. 711, the expectations from an application point of view were evidently not fulfilled because of insufficient stability of the complex. The influence of the constitution of the complexes on their stability can be summarised in the following rules—

Complexes linked according to the spiran configuration are less stable than those forming with the metal atom strain-free two-ring systems [30]. Increased negative charge reduces stability towards acids. Finally, unsymmetrical complexes are less stable than symmetrical ones.

CONSTITUTION OF IRGALAN DYES

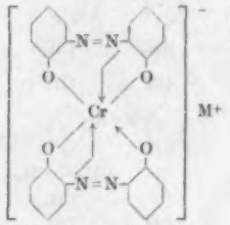
It has been shown that the relationship between chemical constitution and dyeing properties is a complicated matter. An attempt to show how Irgalan dyes fulfil the conditions required is made below.

By omitting sulphonic acid groups in chrome complexes of type (XI), one negative charge is eliminated and the complex becomes symmetrical. As expected, this increases the stability towards acids. Such complexes represent salts of monobasic acids of general formula XIII in which M+ represents a univalent cation. The composition of such complexes was published originally by Drew and Fairbairn [1].



(XIII)

This structurally most simple and previously unknown 2 : 1 chromium complex of 2:2'-dihydroxyazobenzene (XIV) forms the basis of the following considerations*. It appears to fulfil the desired conditions listed above†. The only hydrophilic group present is the co-ordinately linked hydroxyl ion‡.



(XIV)

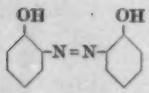
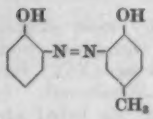
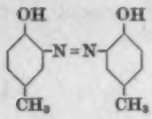
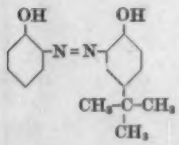
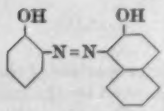
The hydrophilic properties of the chromium atom are completely removed by the stable occupation of all its coordinate valencies. Wool dyeings made with such dyes no longer react with chromable dyes. The dye of formula XIV has very good water solubility and exhausts from an acetic acid or neutral bath non-selectively in brownish-red tones. Its degree of exhaustion from a neutral bath as well as its fastness to wet treatments is, however, far short of the "Irgalan Standard" to be defined further below.

A stepwise increase of the molecular weight increases the fastness to wet treatment as well as the degree of exhaustion from a neutral bath, and when a molecular weight of about 600 is reached the tinctorial properties of Irgalan dyes are obtained (Table IV).

From the above results it might be concluded that the degree of exhaustion and fastness to wet treatments are simple functions of the molecular weight, and thus it would appear that all that would now be necessary was to obtain further 2 : 1 complexes of a different colour by suitable variation of the chemical structure while maintaining approximately constant molecular weight. Only small differences exist between the molecular weights of dyes XVII and XVIII shown in Table IV. The fastness to wet treatment is practically equal. However, there is a considerable difference in the rate of exhaustion. Dye XVIII

* The complexes to be described in the following text are in the majority of cases analytically pure products.
† The complex examined was the potassium salt containing one molecule of water of crystallisation.
‡ According to the rule of mesomerism, it cannot be assumed that one of the four hydroxyl groups has a special function as indicated in the limiting formula XIV.

TABLE IV*

No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°c.	Heavy Milling (staining on wool)	Colour on Wool	Absorption Maximum ($m\mu$.)
XIV		477	36	1	Brownish red	507
XV		505	30	2	Bordeaux	522
XVI		533	24	3	Red-violet	532
XVII		589	12	4–5	Bordeaux	520
XVIII		577	6	4	Violet	545

* For experimental details see section entitled "Irgalan Standard" (p. 722).

exhausts just twice as quickly as dye XVII. The rate of exhaustion and the fastness to wet treatments therefore cannot be related in a simple and direct manner. Whilst the fastness to wet treatment seems to be proportional to the molecular weight, other considerations govern the rate of exhaustion in relation to molecular weight.

In order to be useful in practice, it is absolutely necessary to have good water solubility of the dyes. Whilst dyes XIV–XVII are in part still quite soluble in water, dye XVIII approaches the limit of practically desirable solubility. If this dye contains salt, an impurity hardly avoidable in technical manufacture, it becomes practically insoluble†.

Although the alkali-metal salts of all 2 : 1 chromium complexes are in principle wool dyes with good exhaustion properties, they are in general not suitable for textile dyeing on account of their low solubility, particularly in presence of extraneous ions. They have, however, found application in the colouring of lacquers [16, 22] on account of their pronounced low solubility in water and good solubility in certain organic solvents.

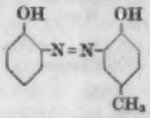
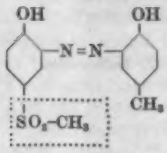
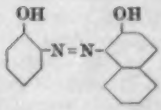
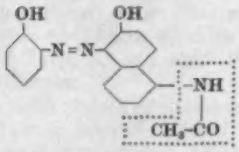
In order to obtain water solubility, non-ionising groups have to be introduced, which nevertheless convey adequate solubility in water without giving too hydrophilic a character to the entire complex molecule. A number of such groups have already been discussed, and the mechanism according to which they are able to associate water has been mentioned. The investigation of these groups in 2 : 1 chromium complexes without sulphonic acid groups has shown, as expected, that all these hydrophilic groups reduce the rate of dyeing, as may be seen in Table V.

When a definite rate of exhaustion is desired, it is found that each of the hydrophilic groups quoted above demands, according to its position in the molecule and according to the presence of other substituents, a minimum molecular size of the dye complex. It has, however, become apparent that only a few groups are suitable for conferring sufficient water solubility on a molecule of the required size and maintain solubility when the dye contains salt. As mentioned above, the presence of some salt is practically unavoidable in technical dye manufacture.

In the first instance, we would mention non-ionic sulphonyl groups as solubilising agents, particularly the sulphones. Alkylsulphonyl groups are more suitable than aryl sulphones, and it has become apparent that within the range of alkyl sulphones the methylsulphonyl group occupies a position of special importance. During the investigation of sulphone groups in the most widely varying combination the methylsulphonyl

† In individual cases it is possible to obtain very fine dispersion of such types of dye by means of suitable dispersing agents and to dye the wool from such dispersion [21]. In most cases such dispersions are, however, very sensitive to pH, stain the dyeing machinery, and frequently lead to dyeings not fast to rubbing. Furthermore, they are unsuitable in package dyeing, where packages act as a filter.

TABLE V

No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°c.	Colour on Wool	Absorption Maximum (mμ.)
XV		505	30	Bordeaux	522
XIX		661	ca. 120	Red-brown	475 (530)
XVIII		577	6	Violet	545
XX		691	24	Greyish violet	545

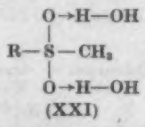
group has shown statistically by far the greatest suitability. This position of special importance may be gathered by reference to the water solubility of alkyl *p*-chlorophenyl sulphones (Table VI).

TABLE VI

Solubility of $Cl{\cdot}C_6H_4{\cdot}SO_2{\cdot}R$

R	Solubility at 85°c. (g./100 ml.)
$-CH_3$	1·43
$-CH_2{\cdot}CH_3$	0·38
$-CH_2{\cdot}CH_2{\cdot}CH_3$	0·30
$-CH(CH_3)_2$	0·49

Methyl phenyl sulphone shows the solubilising properties of the methylsulphonyl groups even better. 100 ml. of boiling water dissolves 7 g. of sulphone. The sulphone does not act as an acid; its solubilising properties are therefore based upon the covalent association of water at the sulphonyl oxygen atoms (XXI).



(XXI)

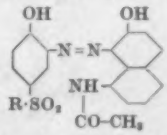
The electron-repelling methyl group strongly increases the tendency towards formation of covalent linkages exhibited by the lone electron pairs in the oxygen atom of the sulphonyl group. The relatively high decrease in solubility which occurs when methyl is replaced by ethyl is due to the methylene group ($>CH_2$) in the ethyl linkage, which lowers the electron drift issuing from the methyl group. This "damping" effect expressed as a function of the number of carbon atoms in the radical shows exponential, not linear, variation. Therefore the difference in effectiveness between methyl and ethyl sulphone is considerably greater than between ethyl sulphone and the higher non-branched homologues. Accordingly, *iso*-propyl sulphone comes between methyl and ethyl sulphone in activity, since with *iso*propyl sulphone two methyl groups act upon the sulphonyl oxygen atom and the effect is only damped by the single $>CH-$ group. These considerations also explain why the solubilising properties in diaryl sulphones are strongly reduced and even practically eliminated by the electron drift towards the aromatic nuclei.

The high hydrophilic value of the methylsulphonyl group causes a decrease in the rate of exhaustion compared with complex dyes containing ethylsulphonyl groups (Table VII).

Of particular significance is the comparison of dye XXIII with the isomeric methylsulphonyl dye. When the ethylsulphonyl group is replaced by vinylsulphonyl, the exhaustion rate decreases markedly (Table VIII). The vinyl group has been mentioned earlier as hydrophilic.

TABLE VIII

2 : 1 Cr Complex of



No.	R	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°c.	Absorption Maximum (mμ.)
XXIV	$-CH_2{\cdot}CH_3$	875	25	580
XXV	$-CH{:}CH_2$	871	128	580

TABLE VII

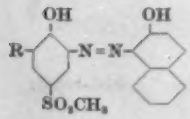
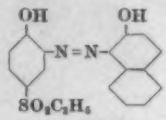
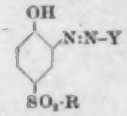
No.	2 : 1 Cr Complex	R	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XXII		H	733	11·5	Dull violet	570
		CH_3	761	12·7	Violet	552
XXIII		—	761	6	Dull violet	552

TABLE IX

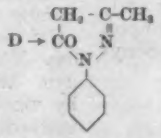
2 : 1 Cr Complexes of

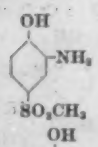
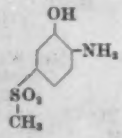


No.	R	Y Radical of	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XXVI	$-CH_3$	1-Phenyl-3-methyl-5-pyrazolone	40	Orange	477
XXVII	$-NH_2$	1-Phenyl-3-methyl-5-pyrazolone	69	Orange	480
XXII	$-CH_3$	2-Naphthol	11·5	Dull violet	570
XXVIII	$-NH_2$	2-Naphthol	23·5	Dull violet	555
XXIX	$-CH_3$	1-Acetamido-7-naphthol	36	Grey	573
XXX	$-NH_2$	1-Acetamido-7-naphthol	58	Grey	580

TABLE X

2 : 1 Cr Complexes of the Azo combinations



No.	D	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XXVI		792	40	Orange	477
XXXI		792	29	Scarlet	490

This relationship shows how the rate of exhaustion is to a large degree dependent upon the nature of the solubilising sulphonyl residue. When in complex dyes of similar structure the methylsulphonyl group is replaced by the sulphamyl group $SO_2{\cdot}NH_2$, which has similar solubilising properties, a considerable decrease in the rate of exhaustion can be noted (see Table IX).

Since a uniform rate of exhaustion was demanded from the individual members of the new dye series, as will be shown in detail in a later section, and since in order to obtain a colour range the different substituents and groupings will have to be inserted like building blocks into the complex dye molecule, it becomes impossible to predict accurately in each individual case either the solubility or the exhausting power. The physical and chemical properties of such compounds are not simple additive functions of the properties of the substituents they contain. For example, no accurate measure of hydrophilic effect can be ascribed to the methylsulphonyl group. Its mode of action depends within wide limits upon its position in the nucleus (see Table X) and upon the presence of other substituents.

However, with the aid of the formulae shown on pp. 710–711 it is possible, within certain limits, to form a qualitative estimate of the influence of substituents on the exhausting power of the dye and to gain an insight into their mode of action. As an example, a decrease of exhausting power occurs in general when an NH·CO group enters the structure (see Table V, dyes XVIII and XX, also Table XI).

The mode of action of the acylamino group becomes evident where its amide hydrogen is able to lose its hydrophilic character by formation of an intermolecular bridge (chelation). Thus the rate of exhaustion increases strongly on rearrangement of the acylamino group of dye XXXII into the "chelate position" (dye XXXIII) in Table XII.

The assumed chelation in dye XXXIII shows in contrast to the isomeric non-chelated compound not only increased rate of exhaustion but also has considerable bathochromic effect [33].

All these phenomena are not limited to *oo'*-dihydroxyazo dyes but are true in principle for all classes of dyes. Where the properties of the fundamental prototype differ in principle, the above phenomena may, however, become less recognisable. For example, very marked differences exist between the complex dyes of the *oo'*-dihydroxyazo, the *o*-hydroxy-*o'*-carboxyazo, and the *oo'*-dihydroxyazamethin series (Table XIII).

This comparison gives rise to the assumption that exhausting power is decisively dependent

TABLE XI

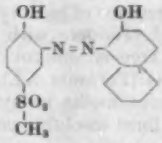
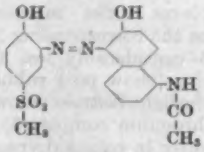
No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XXII		733	11·5	Brown–violet	570
XXXII		847	300	Greyish violet	555

TABLE XII

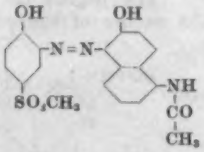
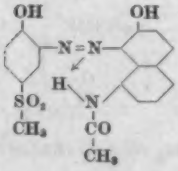
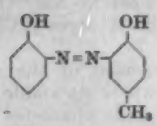
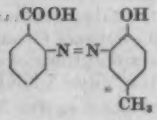
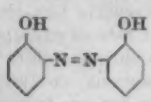
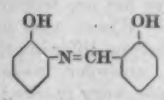
No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XXXII		847	300	Greyish violet	555
XXXIII		847	36	Blue–grey	573

TABLE XIII

No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
XV		505	30	Bordeaux	522
XXXIV		561	73	Red-brown	335 (522)
XIV		477	36	Brownish red	507
XXXV		475	ca. 60	Greenish yellow	447

on aromatic character, i.e. on the capabilities of resonance within the entire dye molecule.

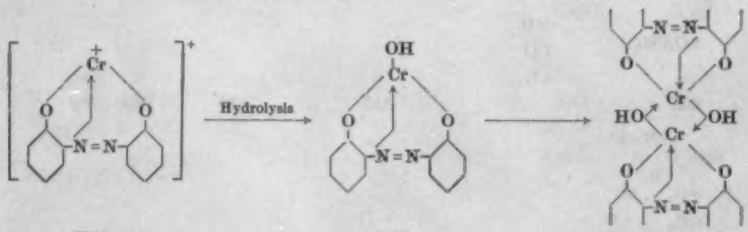
In the fundamental form of the *oo'*-dihydroxyazo series resonance possibilities exist within four strain-free ring systems (in Formula XXXVI the resonance space is shown shaded).

(XXXVI)

An increase in size of the resonance system increases the rate of exhaustion. Table XIV gives a number of pertinent examples of this. Since with increased resonance space a deepening of colour does occur, the rough rule may be formulated that more heavily coloured compounds exhaust better than the lighter ones of similar nature (cf. compound XXVI with XXXI, Table X; XIV with XXXV, Table XIII).

Several processes have been published in the literature for the preparation of chromium-complex dyes free from sulphonic acid groups. Those of importance employ metallising with aqueous salicylatochromiates [2, 21(c), 34], also metallising with tervalent chromium salts in formamide [35] or with chromates in alkaline aqueous media in presence of reducing carbohydrates [36]. In none of these processes can the uniform formation of 2 : 1 chromium complexes be guaranteed, since this depends entirely on the constitution of the dye to be metallised and upon the reaction conditions. Each single case requires, therefore, special study, and success is largely dependent on the quality of the analytical methods evolved. Faulty chromation may yield mixtures of 2 : 1 chromium complexes with unchromed dye or with 1 : 1 complexes. The presence of both types of impurity results in chromed products with inferior dyeing properties. 1 : 1 Dye–chromium complexes are salts of dye cations (Formula XL). They tend to hydrolyse in aqueous media to hydroxides (XLI) and eventually to form insoluble polymers (XLII).

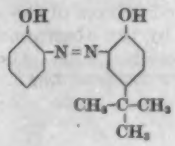
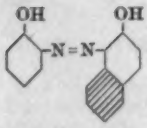
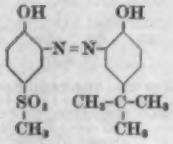
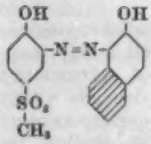
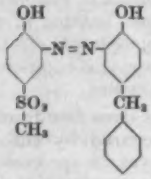
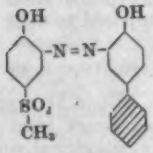
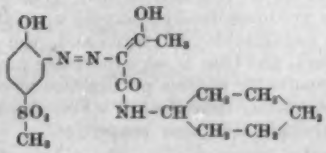
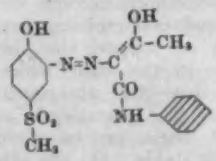
1 : 1 Complexes differ markedly in dyeing behaviour from the corresponding 2 : 1 complexes. They exhaust considerably less from a neutral bath, the dyeings show poor rubbing and milling fastness, and the light fastness is lower. In relation to the 2 : 1 chromium complexes, they are purer in hue and lighter in colour (hypsochromic). The absorption graphs are more or less different (e.g. Fig. 3 and 4), which is an indication that in the 2 : 1 complexes some resonance exists between the two dye molecules standing at right angles towards one another [37]. The degree of this resonance depends on the nature of the colouring matter present.



(XL) (XLI) (XLII)

TABLE XIV*

(The newly added resonance space is shown shaded)

No.	2 : 1 Cr Complex of	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°c.	Colour on Wool	Absorption Maximum (mμ.)
XVII		589	12	Bordeaux	520
XVIII		577	6	Violet	545
XIX		745	ca. 120	Red–brown	475 (530)
XXII		733	11·5	Brown–violet	570
XXXVI		813	15	Brownish bordeaux	(335) 525
XXXVII		785	10	Brownish bordeaux	538
XXXVIII		831	49	Greenish yellow	440
XXXIX		819	25	Reddish yellow	452

* Cf. XVII with XVIII with XIXXXII, XXXVI with XXXVII, and XXXVIII with XXXIX.

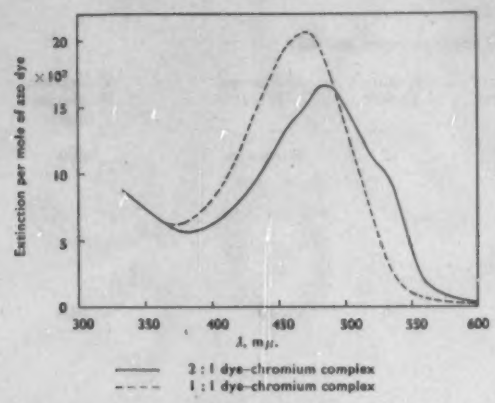


FIG. 3—Absorption Spectra of Dye–Chromium Complexes for Irgalan Orange RL

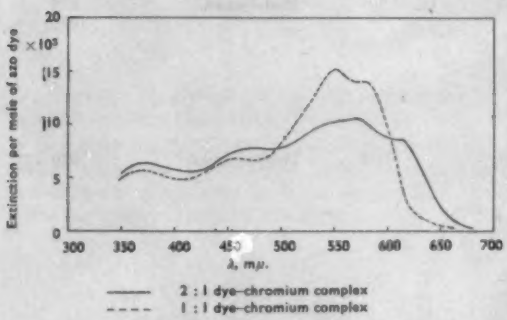


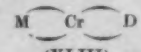
FIG. 4—Absorption Spectra of Dye–Chromium Complexes for Irgalan Brown Violet DL

The two-dimensional 1 : 1 chromium–dye complexes have in contrast to the 2 : 1 complexes some affinity for vegetable fibres and for acetate rayon. As in the case of 1 : 1 complexes containing sulphonic acid groups, the unsaturated character of the chromium atom in the unsulphonated 1 : 1 complexes can be shown by overdyeing with metallisable dyes (Table XV).

TABLE XV

Dye	Colour on Wool	Colour on Wool after overdyeing with Eriochrome Azurole B
Neutral Orange RX (no complex)	Orange	Orange–brown
2 : 1 Cr complex of XXVI	Orange	Orange–brown
1 : 1 Cr complex of XXVI	Orange	Brown–violet

The addition of a further metallisable system to unsulphonated 1 : 1 chromium complexes can also be carried out in substance. In this manner unsymmetrical complexes (XLIII) are formed in which D represents the residue of the 1 : 1 complex and M represents the associated complex-forming group. In this case M may represent a colourless



(XLIII)

compound; e.g. when using *o*-hydroxycarboxylic acids, dye types of general formula XII are formed. Alternatively, M may represent a complex-forming substance with dye character. In the latter case mixed complex dyes result, the colours of which differ from the equimolecular mixtures of symmetrical 2 : 1 complexes of the single component. This is shown by the absorption spectra (Fig. 5).

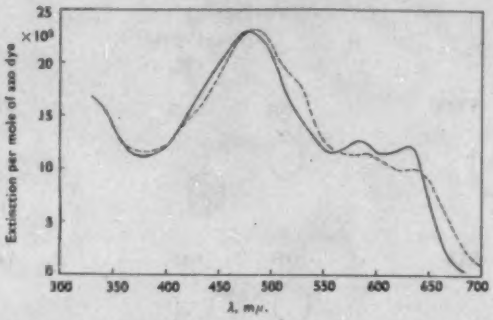


FIG. 5—Comparison of the Absorption Spectra of a Homogeneous Chromium Complex "Mixture" G–Cr–O (solid line ——) and an Equimolecular Mixture of Symmetrical 2 : 1 Complexes of G–Cr–G and O–Cr–O (dotted line – – –) (G = Irgalan Grey BL Base; O = Irgalan Orange RL Base)

As indicated above, unsymmetrical chromium complexes are less stable than symmetrical ones. The stability of chromium-complex types of formula XLIII depends within wide limits upon the nature of the component groups D and M. In each case there is, however, the tendency towards disproportionation into symmetrical compounds; i.e. after prolonged heating of a neutral aqueous solution of the complex G–Cr–O the symmetrical complexes of the single components G and O can be shown to be present.

Mixed complex dyes free from sulphonic groups may also be prepared by chroming mixtures of two different dyes, a process which was first described for the preparation of lacquer dyes[88] and which is supposed to take place according to the equation—

$$D^1 + D^2 + Cr^{3+} \rightarrow D^1\text{–}Cr\text{–}D^2$$

In this equation D^1 and D^2 represent two different dyes. Of course, apart from the desired mixed complexes, the symmetrical compounds D^1–Cr–D^1 and D^2–Cr–D^2 are also formed. The proportion of these products depends largely upon the nature of the metallisable mixture and the metallising method, and that is why there are practical limits to apparently endless possibilities of combination. Combinations described in a French patent[89] have particularly desirable properties.

In the previous paragraph, we have dealt entirely with chromium-containing complexes. Bivalent ions such as copper, zinc, and manganese are unsuitable in this case, since with metallisable azo dyes they yield uncharged complexes of low solubility. The complexes of the coordinate sexivalent ferric and aluminium ions are not sufficiently stable. On the other hand, unsulphonated 2 : 1 cobalt complexes have similar

stability to the chromium complexes [40]. In contrast to the chromium complexes, they are more hypsochromic. Most of them exhaust somewhat less rapidly from a neutral bath and they are faster to light (Table XVI). Their rate of exhaustion appears to bear a different relation to temperature from that shown by the chromium complexes*.

TABLE XVI

2 : 1 Complexes of 3-Amino-4-hydroxyphenyl Methyl Sulphone diazotised and coupled with 2-Naphthol

Complex-forming Metal	Mol. Wt. of Complex Acid	$t_{\frac{1}{2}}$ (min.) at 90°C.	Colour on Wool	Absorption Maximum (mμ.)
Cr	733	11·5	Brown-violet	570
Co	740	21	Bordeaux	550

The preparation of 2 : 1 cobalt complexes free from sulphonic acid groups is simpler in principle than that of the chromium complexes, since they are readily formed by heating with cobaltous salts in aqueous solution [41]. On the other hand, because cobalt has two stable valency stages, the possibility of formation of undesirable by-products (such as 1 : 1 cobaltous, 1 : 1 cobaltic, and cobaltous salts of the 2 : 1 cobaltic complexes) is greater than with the chromium complexes.

PHYSICAL PROPERTIES OF THE 2 : 1 CHROMIUM COMPLEXES

The aqueous solutions of alkali-metal salts of the 2 : 1 chromium complexes which have been discussed react neutral. They are thus salts of strong acids, which can be shown also by means of neutralisation graphs of the complex acids. Fig. 6 shows the neutralisation graph of Irgalan Orange RL complex acid in a mixture of water and ethylene glycol monomethyl ether. For the sake of comparison the neutralisation graph for an equimolecular quantity of hydrochloric acid is also shown. The two curves are practically coincident; i.e. in dilute solutions the complex acid shows complete dissociation.

The complex acids have extremely low solubility in water. The nature of the cation has a great influence upon the water solubility, the ammonium salts in general being less soluble than the sodium or potassium salts. The salts of higher fatty amines are insoluble in water. Incomplete investigations tend to show that at 90°C. the alkali-metal salts of 2 : 1 chromium complexes are molecularly dispersed in water, whilst at room temperatures they are strongly aggregated. In consequence, cooling solutions of Irgalan dyes show a more or less pronounced Tyndall effect.

DYEING PROPERTIES OF IRGALAN DYES

The Irgalan Standard

This comprises a series of properties which are to be attained by dyes to be incorporated in the Irgalan range.

Perhaps the most important property of the Irgalans is their non-selective dyeing of differing wool qualities and hence their ability to yield level dyeings without skitteriness.

* This has not been investigated fully.

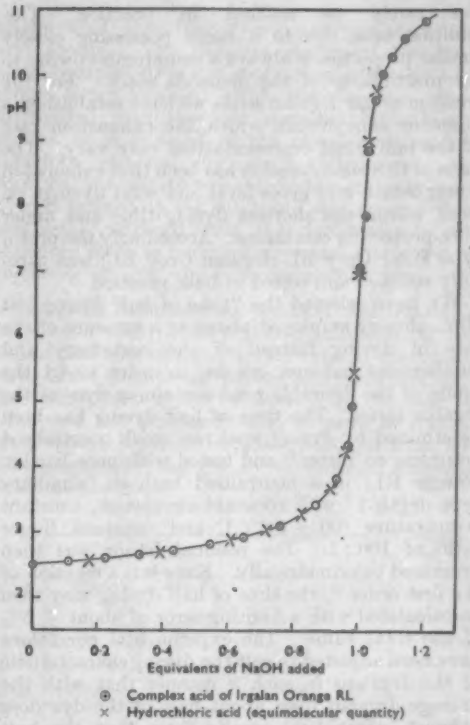


FIG. 6—Titration Curve of the Complex Acid of Irgalan Orange RL in a Mixture of Methyl Cellosolve and Water

When fibre sections of a variety of wool dyeings, which to the eye appear solid and level, are examined under the microscope, a certain degree of irregularity will always be found. Up to a certain degree of skitteriness dyed wool appears level to the human eye. All Irgalan dyes are within this limit. In the section dealing with relationship between constitution, non-selective exhausting power, and acid requirement of wool dyes, it has been shown that lower exhausting power produces greater tendency to skittery dyeing. 2 : 1 Metal complexes not containing sulphonic acid groups yield level dyeings within wide limits of exhaustion power. However, when combining complex dyes having very strongly differing exhausting properties skittery dyeings are more likely the more individual dyes differ in colour. This is due to polychroic dyeing caused by the different affinity of the individual dyes having different exhaustion power. Thus, the dyeings not only show variations in depth of colour but also differences of colour tone on individual fibres. It is well known that eyes trained in colour vision react more strongly towards differences in hue than towards mere differences of depth. Thus dyes which are to be combined at will with one another under dyeing conditions protecting the wool fibre should display similar dyeing characteristics.

Completely equal exhausting power of a group of dyes in addition to certain high fastness properties

can rarely be realised in practice. The addition of a dye to a range possessing closely similar properties is always a compromise owing to the multiplicity of the demands made. For the creation of the Irgalan series we have established a range or zone within which the exhaustion rate of the individual representatives may vary. The basis of this consideration has been that exhaustion power which still gives level and solid dyeings on cloth within the shortest dyeing time and under fibre-protecting conditions. Accordingly the prototype Polar Grey BL (Irgalan Grey BL) was carefully selected and tested in bulk practice.

We have selected the "time of half dyeing" at 90°C. already employed above as a measure of the rate of dyeing instead of the customary and cumbersome exhaust graphs, in order to fix the limits of the desirable zone containing dyes of the Irgalan series. The time of half dyeing has been determined by dyeing wool raw stock (neutralised according to Lister [42] and tested with pure Irgalan Orange RL) in a neutralised bath in "auxiliary type depth 1" with constant circulation, constant temperature (90 ± 0·2°C.), and constant liquor ratio of 100 : 1. The residual liquor was then examined colorimetrically. Since it is a reaction of the first order [43], the time of half dyeing may then be calculated with a limiting error of about ± 5% of the total value. The experimental conditions have been adjusted to suit the dyeing characteristic of the Irgalans in such a manner that with the average Irgalan dyes about half of the dye does exhaust. Statistical results show that the best possibility of combination amongst complex dyes with Irgalan Grey BL exists when the time of half dyeing of the shading dyes lies within the range of 9–20 min. (Table XVII).

TABLE XVII

Times of Half Dyeing of Irgalan Dye at 90°C. and pH 7

	(min.)		(min.)
Yellow GL	28	Brown Violet DL	11·5
Yellow 2RL	11·3	Brown 7RL	8
Orange RL (chemically pure)	10·7	Dark Brown 5R	8·5
		Brown 2GL	13
Red 4GL*	9	Brown 2RL	15
Red 3G	10·4	Brown 3BL	14·6
Red 2BL*	9	Blue RL*	19
Bordeaux 2BL	8·5	Blue GL	11·9
Rubine RL	12	Grey BL	16·8
Violet 5RL	11·5	Olive BGL	13·7
Violet 4BL	11	Brilliant Green 3GL	22·5

* Not yet on the market

Apart from the uniform exhausting power the Irgalan dyes have, as desirable for their end-use, a high and uniform level of fastness, the lower limit of which is defined by the following E.C.E. ratings—

Light fastness	at least 6
Fastness to heavy milling	at least 4–5
Fastness to perspiration	4
Fastness to rubbing	5

Solubility at least 40 grams per litre in soft water at 90°C.

Generally speaking, the Irgalan dyes have better solubility and fastness to light than the values given above.

RELATION BETWEEN RATE OF EXHAUSTION AND DYEING CONDITIONS

The rate of exhaustion of the Irgalan dyes depends upon temperature, acidity of the dyebath, and the presence of additions to be described below.

The relation of exhausting power and temperature of Irgalan dyes differs from that of the metal-free sulphonic acid neutral-dyeing dyes by showing less decrease of the exhaustion with decrease in temperature. Fig. 7 shows the rate of exhaustion of Irgalan Orange RL and Polar Brilliant Blue GAW, an acid anthraquinone dye, as a function of temperature.

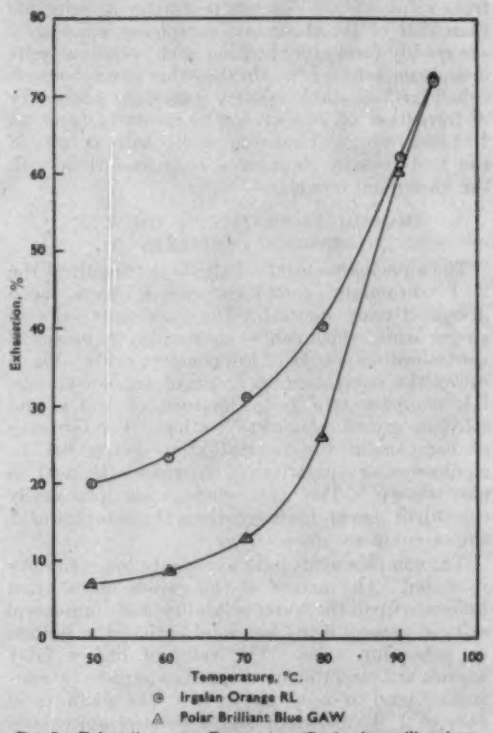


FIG. 7— Exhaustion *versus* Temperature (Dyeing in auxiliary type depth 1 for 15 min. at pH 7 and liquor ratio 100 : 1)

It has been shown in preliminary investigations* that the rate of exhaustion of the Irgalans at lower temperatures is only apparently high, since much dye is initially merely adsorbed on to the surface of the wool fibre. This adsorbed dye is related to the "strike" of the Irgalans, the significance of which has already been reported by H. R. Hirsbrunner [44].

Preliminary investigations* have shown that the effect of variations in pH on the exhaustion of Irgalan dyes is different from their effect on the exhaustion of sulphonated neutral-dyeing wool

* A further report on these incomplete investigations is planned.

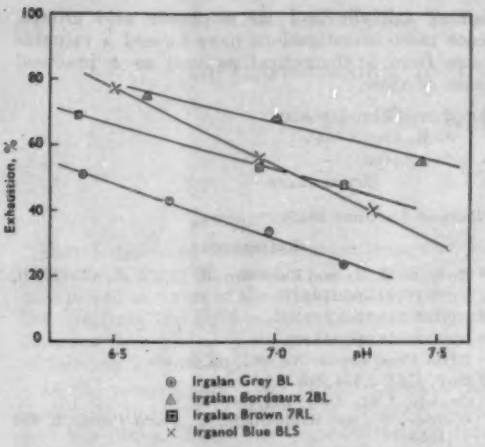


FIG. 8— Relation between Exhausting Power and the pH of the Dye Liquor (Dyeing for 15 min. in auxiliary type depth 1 at 90°C. and liquor ratio 100 : 1)

dyes not conteining a metal in complex union. Fig. 8 shows the exhaustion characteristics of Irgalan Bordeaux 2BL, Irgalan Brown 7RL, and Irgalan Grey BL, as well as Irganol Blue BLS, which is a sulphonated wool dye.

These results prove that the Irgalan dyes are less sensitive to differences in electric charge of the wool fibre than dyes containing sulphonic acid groups. The negative charge of the 2 : 1 metal-complex dyes not containing sulphonic acid groups is not localised within the molecule. It is distributed over the four metallisable hydroxyl groups, or is situated at the metal atom and is therefore screened by steric hindrance. By contrast, the negative charge in the ordinary wool dyes is located at the sulphonic acid anion. It is completely exposed, and the dye molecule can therefore react to every electrostatic attraction or repulsion without any protection whatever.

Inorganic salts such as common and Glauber's salts have often a very strong influence on the exhaustion rate of Irgalan dyes even in concentrations lower than those causing aggregation of dye. An initial drop in the exhaustion in the case of Glauber's salt (shown in Fig. 9) may be due to electrostatic repulsion of the dye anion from the wool negatively charged by entrance of sulphate ions into the fibre.

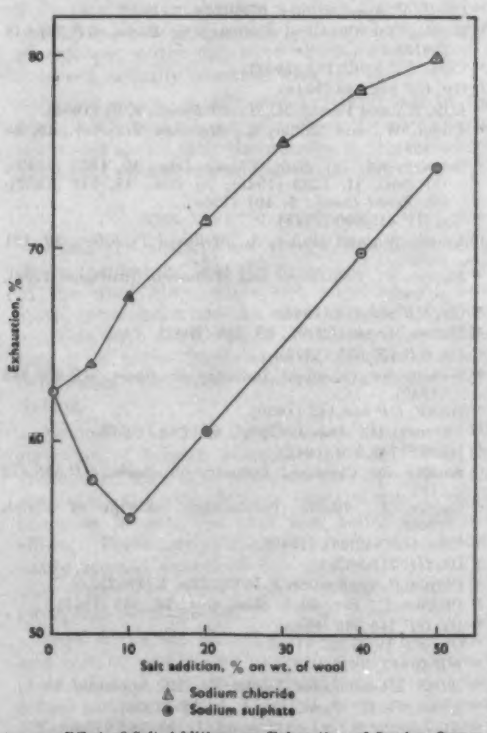


FIG. 9— Effect of Salt Additions on Exhaustion of Irgalan Orange RL (Dyeings made with chemically pure Irgalan Orange RL in auxiliary type depth 1 at 90°C. and pH 7, liquor ratio 100 : 1)

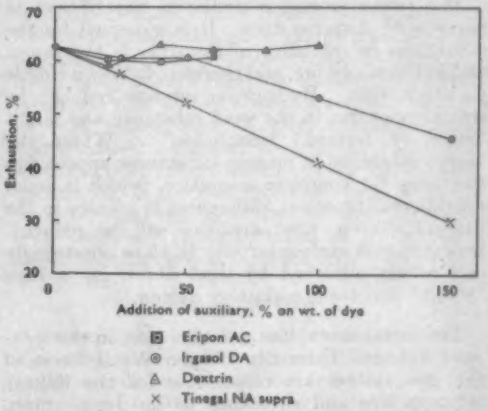


FIG. 10— Effect of Standardising and Retarding Agents (Eriopon AC, etc.) on the Exhaustion of Irgalan Orange RL (Dyeings with chemically pure Irgalan Orange RL in auxiliary type depth 1 at 90°C. and pH 7, liquor ratio 100 : 1)

Fig. 10 shows the influence of Tinegal NA and Irgasol DA, which are recommended as retarding agents. In the same figure it is shown that dextrin and Eriopon AC do not influence the exhausting power of Irgalan dyes.

The migrating capacity of Irgalan dyes at the boil is noticeably high in comparison with neutral-dyeing wool dyes not containing metals (see Table XVIII). Evidently, this is an expression of the solubility ratio dye–water/dye–wool (see below), and the poor fastness to potting of Irgalan dyes as well as their good penetrating power may at least be partly due to the migrating power of these dyes.

A noticeable difference between Irgalan and acid wool dyes is that the former show within narrow limits constant light fastness when applied to the most diverse substances such as silk, wool, nylon, Perlon, acetate rayon, and lacquers.

TABLE XVIII

Migration* of Irgalan Dyes in comparison with Metal-free Milling Dyes (Polar Dyes)

Irgalan Dyes	(%)*	Polar Dyes	(%)*
Yellow GL ...	21	Yellow G	15
Yellow 2RL ...	30	Orange GS	15
Orange RL... ...	24	Red GRS	10
Rubine RL ...	20	Red B	18
Violet 4BL ...	20	Brilliant Red 10B ...	20
Brown Violet DL ...	40	Brilliant Blue GAW ...	10
Grey BL	25	Blue 4GL	3
Brown 7RL ...	35	Green B	15

* % Dye migrated from the fibre into the bath after 90 min. boiling in the presence of 10% Glauber's salt crystals plus 2% ammonium sulphate.

Dyeing Mechanism

From the behaviour of Irgalan dyes described in this paper we have made the following deductions concerning the dyeing mechanism of 2 : 1 metal complexes free from sulphonic acid groups—

The dyeing process is similar to that of acetate rayon with disperse dyes. It is governed by the differences in solubility of the dyes in the liquor and in the wool fibre, and therefore follows a simple partition rule. Hydrophilic groups reduce the solubility of dye in the wool substance and might better be termed "lanaphobic". Where the higher solubility in protein substances approaches the value for complete saturation (which is equal for different proteins), differences in affinity in the case of diverse wool qualities will be reduced. Owing to high surface activity Irgalans are strongly and evenly adsorbed by wool fibres; i.e. a high "strike" denotes non-skittery dyeing.

The metal atom does not take part in the dye–wool linkage. Primarily van der Waals forces of the dye system are responsible for the linkage between dye and substance to be dyed. Since within the aromatic dye molecule there is resonance, these forces are mobile and may adapt themselves according to the various linkage possibilities of the substrate. It cannot yet be estimated how far the anionic character of the 2 : 1 metal-complex dyes may contribute to their linkage with protein substances. The suggestion that formation of salts between dye and ammonium cations of the wool substance does take place and that such salts have a low solubility in water may explain to some extent the high wet fastness properties of these dyes.

* * *

The author expresses his thanks for the assistance of his collaborators, Messrs. Hans Ackermann, Fabio Beffa, Walter Biedermann, and Werner Kuster. Thanks are due also to Messrs. H. R. Hirsbrunner, E. Schmid, C. Soiron, W. Stocker, and E. W. Thommen, who collaborated in the field of practical dyeing problems of the Irgalan dyes.

In this connection special mention should again be made of the quoted work of O. Schmid and A. Conzetti concerning chrome-complex dyes containing salicylic and no sulphonic acid groups, since these investigations have formed a valuable basis from a theoretical as well as a practical point of view.

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EXPLANATORY PAPER ON MODERN THEORY

An Introduction to the Theory of Wool Dyeing

II—The Kinetic Approach*

L. PETERS

INTRODUCTION

Part I described the equilibrium theory of the affinity of dyes for wool[1]. The affinity was interpreted in terms of the work needed to remove the dye from the fibre under specified conditions. This was then related to the more practical concept of fastness to washing.

In the present paper, the kinetic aspect is first dealt with in terms of the rate of diffusion of dye into the fibres, that being regarded as the rate-determining step in the process of combination. The time of half-dyeing and the time to reach higher degrees of saturation are shown to be related to the diameter of the fibres or the quality of the wool by what is called the *diffusion coefficient*. The influence of the ultimate degree of exhaustion of the dyebath is also described.

The concept of *activated* diffusion is then explained and a description is given of the "activation energy" barrier, which should really be called the *heat of activation*. This barrier determines the influence of temperature on the rate of diffusion. By means of a mechanical analogy the concept of *entropy* is illustrated, and it is shown how, because of entropy, a dye can have affinity even when it does not actually combine with the fibre.

Consideration of diffusion into and out of the fibres leads to a clearer picture of the equilibrium state and shows that the affinity is the difference between two activation free energy barriers.

THE KINETIC APPROACH

When the equilibrium theory was dealt with, it was pointed out that the shape and the structure of the wool fibre, while not affecting the final state, must influence the rate at which dye can combine with the keratin. This rate of combination is of prime importance in practice, since it determines the time required for satisfactory dyeing.

According to the detailed knowledge of the structure of keratin fibres, accumulated over the years, each fibre is so complex that to analyse the details of the rate process exactly would be an immense labour, the task not being worth the effort. Fortunately, little accuracy is lost, and easily applied equations are obtained, by making the following reasonable, though somewhat sweeping, assumptions.

Wool fibres are almost circular in cross-section and can be treated as uniform solid cylinders if their internal cellular structure is ignored. Any actual sample of wool, however, contains fibres of different diameters, the values being spread over a range determined by the accuracy of the sorting and blending. Nevertheless, such variation in diameter is usually ignored (although in a badly blended batch of wool it might cause two-tone effects), and all the fibres are assumed to have the same diameter. The dye acid is regarded as soluble in the wool keratin, exhaustion of the dyebath being assumed to be due to the far greater solubility of dye in the fibre than in water. In scientific jargon, the dye is said to have a high partition ratio between keratin and water, i.e. the ratio of its solubility in keratin to that in water is high.

The dye is not simply dissolved in the fibre—even the Donnan theory does not assume this for hydrogen ions, although it does so for anions of low affinity— but, surprisingly enough, no serious discrepancy arises if complete solubility is assumed. Assuming that all but a small fraction is adsorbed at sites makes little, if any, difference to the mathematical approach so long as the amount adsorbed is a constant fraction of the total adsorbed at sites or on the surface. The word "*ad*sorbed" means "combined *on* to sites or *on* to a surface", and "*ab*sorbed" means "taken *in* to the fibre", *sorbed* being a general term for both.

THE SQUARE ROOT LAW

Assuming that dyeing is a process in which the dye acid merely diffuses into fibres which are uniform cylinders all with the same diameter, then the rate of dyeing can be shown to obey certain simple laws. Consider a sample of wool suddenly immersed in a solution of a dye acid: if the amount of dye going into the wool in the first minute is small, then according to the laws of diffusion we can expect twice as much to be on after 4 min., three times as much after 9 min., four times as much after 16 min., and so on, provided that the equilibrium state is far enough off. This relationship can be expressed in words as follows: the amount of dye taken up is directly proportional to the square root of the time of dyeing. It can also be expressed by the equation—

$$M = K\sqrt{t} \qquad \text{(i)}$$

In this equation M is the weight of dye taken up (expressed on the weight of wool), t is the time the wool has been in the dyebath, and K is a coefficient of proportionality. The value of K is constant in any single dyeing, but its magnitude depends on the temperature and the concentration of the dyebath and on the diameters of the fibres as well as on the acid-combining capacity of keratin.

* Based, in part, on a lecture given to the West Riding Section at the Victoria Hotel, Bradford, on 13th January 1955, Mr. G. B. Angus in the chair.

As dyeing proceeds, equilibrium is approached, and this simple law breaks down, the graph of M against $\sqrt{t}$ ceasing to be a straight line (as equation (i) predicts), and finally curving over to a horizontal limit (see Fig. 1), as it obviously must do if there is to be a final equilibrium state. The value of K can be found from a graph like Fig. 1 by measuring the steepness of the initially straight part. In practice, however, there are errors in applying this method, for the zero of the time-scale is somewhat uncertain because of the time taken for the wool to become thoroughly wetted out.

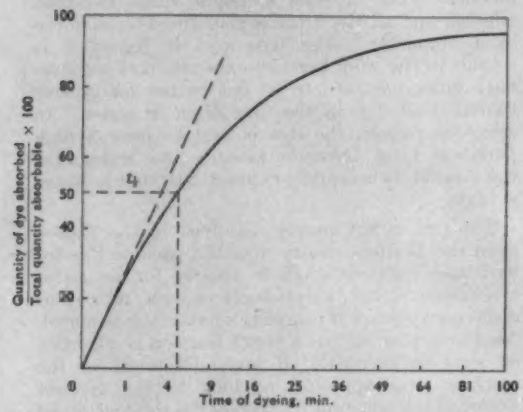

FIG. 1

THE TIME OF HALF DYEING

An easier method of characterising the speed of dyeing is to estimate the time taken for the wool to absorb 50% of what it will ultimately take up—the time of half dyeing, as it is called. Any other percentage could, of course, be chosen, that at 50% being the most easily and accurately measured, and examples are given later of the use of higher percentages, which are of more use in actual dyeing.

THE DIFFUSION COEFFICIENT

The time of half dyeing is not a characteristic of the dye alone, nor does it depend only on the constitution of the material into which the dye is diffusing, for it also includes the effect of the fineness of the wool fibres. Other things being equal, a dye with a time of half dyeing of 1 min. on one sample of wool will have a time of half dyeing of 4 min. on a sample which has fibres twice as thick, or 9 min. if they are three times as thick. There is a constant which characterises the behaviour of the dye in diffusing into wool keratin, independent of the thickness of the fibres, and this is known as the *diffusion coefficient* D. It is related to the time of half dyeing $t_{\frac{1}{2}}$ and the area of cross-section of the fibres A by the equation—

$$D = \frac{A}{50t_{\frac{1}{2}}} \qquad \text{(ii)}$$

the factor 50 arising from an elaborate calculation based on the mathematics of a cylinder and the fact that the concentration of the dyebath is maintained constant.

Once the time of half dyeing is known for wool fibres of a given fineness, the diffusion coefficient is easily calculated. From equation (ii) it follows that on a sample of wool whose fibres are 28 microns (μ.) thick and thus have an area of cross-section—

$$A = \frac{22}{7} \times 14 \times 14 = 616 \text{ sq. microns}$$

a dye whose time of half dyeing is 10 min. will have a diffusion coefficient given by—

$$D = \frac{616}{50 \times 10} = 1{\cdot}23 \text{ sq. microns per minute}$$

We shall find these units the most convenient in the following sections, but it is as well, perhaps, to point out that square centimetres per second are the units usually employed in scientific circles. Since a micron is one-thousandth of a millimetre, and a millimetre is one-tenth of a centimetre, one micron is a ten-thousandth of a centimetre or 10^{-4} cm. and a square micron is $10^{-4} \times 10^{-4}$ or 10^{-8} sq. cm. The above value of D can therefore be written as—

$$D = 1{\cdot}23 \times 10^{-8} \text{ sq.cm./min. or } 2{\cdot}1 \times 10^{-10} \text{ sq.cm./sec.}$$

On the other hand, once the diffusion coefficient is known, it is easy to calculate the time of half dyeing for fibres of any given thickness. Suppose that a dye is known to have a diffusion coefficient of 5×10^{-10} sq.cm./sec. If the wool fibres we are concerned with are 35 μ. thick, they have an area of cross-section—

$$A = \frac{22}{7} \times \frac{35}{2} \times \frac{35}{2} = 962{\cdot}5 \text{ sq.}\mu.$$

It is then best to convert the given diffusion coefficient to sq.μ./min. by multiplying by 10^8 and by 60, giving—

$$D = 3 \text{ sq.}\mu\text{./min.}$$

The time of half dyeing of this dye on such fibres is now simply calculated, since—

$$t_{\frac{1}{2}} = \frac{A}{50D} = \frac{962{\cdot}5}{50 \times 3} = 6{\cdot}4 \text{ min.}$$

EFFECT OF WOOL QUALITY

The thickness of the fibres need not always be known, since, although the quality number of a given batch of wool is not entirely based on the mean fibre diameter (as is asserted in the U.S.A.), the spinner's quality number has been found to be highly correlated with fibre fineness and can, therefore, be used approximately as an index of dyeing properties. In the cross-section of a yarn spun down to the count represented by the spinning quality of the wool, there are about 20 fibres on the average. Consequently, the mean area of cross-section of each fibre A is related to the wool quality Q and the density of keratin. In water, the latter may be assumed to be approx. 1 g./c.c., so that the weight of 1 cm. of yarn will be $20A$ g. Since the worsted count of such a yarn is Q, the weight per centimetre is also—

$$\frac{453{\cdot}6}{560Q \times 36 \times 2{\cdot}54} = \frac{1}{113Q} \text{ g.}$$

These two weights must be equal, from which it follows that—

$$20A = \frac{1}{113Q}$$

or

$$A = \frac{1}{2260Q} \qquad \text{(iii)}$$

Putting this in equation (ii) and rearranging, one obtains—

$$t_{\frac{1}{2}} = \frac{887}{QD} \text{ min.} \qquad \text{(iv)}$$

provided that D is expressed in square microns per minute.

HIGHER-PERCENTAGE DYEING TIMES

From the mathematically calculated curve it can be deduced that a dye which has a time of half dyeing of 10 min. when diffusing from a solution kept at a constant concentration and temperature will take 72½ min. for the fibres to reach 95% saturation, and only after 116 min. will 99% saturation be reached. These figures show how the time of half dyeing can be related to the time needed for satisfactory dyeing under such conditions.

All this is very theoretical, since, in practice, dyebaths are not kept up to fixed strength, but gradually become exhausted as equilibrium is approached. When this happens, the time of half dyeing is different even if the diffusion coefficient is the same, for its value depends on the liquor : wool ratio and the affinity of the dye, i.e. on the value of the ultimate exhaustion of the dyebath. If this is 90%, the time of half dyeing is given by the formula—

$$t_{\frac{1}{2}} = \frac{18{\cdot}2}{QD} \qquad \text{(v)}$$

which can be compared with that previously given (equation iv) for a constant-strength dyebath (zero exhaustion).

In general—

$$t_{\frac{1}{2}} = \frac{k}{QD} \qquad \text{(vi)}$$

where k is a constant which depends on the ultimate exhaustion as given in Table I.

TABLE I

Values of k for Various Values of the Ultimate Exhaustion

Exhaustion (%)	k
0*	887
.	.
30	512
40	416
50	323
60	223
70	129
80	66·0
90	18·2

* i.e. "Infinite" dyebath (constant concentration).

The time to reach other degrees of saturation also depends on the ultimate exhaustion; e.g. a dye whose time of half dyeing is 1 hr. under conditions which give an ultimate exhaustion of 90% would take 51½ hr. to get to 95% saturation, i.e. to—

$$\frac{95}{100} \times 90 = 85{\cdot}5\% \text{ exhaustion}$$

Even to reach 90% saturation, i.e.—

$$\frac{90}{100} \times 90 = 81\% \text{ exhaustion}$$

would take 24½ hr. as shown in Table II.

TABLE II

Times to reach Given Degrees of Saturation

Ultimate exhaustion ... / Saturation	0%*	50%	60%	70%	80%	90%
50% ($t_{\frac{1}{2}}$) ...	1·00	1·00	1·00	1·00	1·00	1·00
60% ...	1·55	1·70	1·74	1·82	1·88	1·94
70% ...	2·31	2·82	2·89	3·16	3·31	3·88
80% ...	3·41	4·58	4·91	5·62	6·15	7·75
90% ...	5·31	8·12	8·92	11·5	14·4	24·5
95% ...	7·25	12·0	13·9	19·1	25·6	51·2
99% ...	11·6	—	—	—	—	—

* i.e. "Infinite" dyebath (constant concentration).

It is clear that the time of half dyeing, while useful because it is easily visualised, must be inferior to the diffusion coefficient as a measure of the dyeing process itself, because the latter is independent of the form of the fibres and of the degree of exhaustion of the dyebath.

DYNAMIC EQUILIBRIUM

When the fibres are first immersed in the dyebath, dye molecules rapidly diffuse into the fibre, but after a time some of them begin to diffuse out again— not as rapidly as those diffusing in, because there are so few inside compared with the number outside. But as more and more accumulate inside, the rate of diffusion back into the solution increases and, as the dyebath becomes more and more exhausted, the rate of diffusion into the fibre decreases. Ultimately, the rate of those entering and the rate of those leaving become equal, and the amount of dye inside then stays constant, when "dynamic equilibrium" is reached. If the wool is then washed with water, there will be no dye outside to diffuse in and, if the process is completely reversible, the dye should now "bleed" out and be completely "stripped" from the fibres. Dyes, however, are chosen for their high affinity, so that even if the process is *theoretically* reversible, the *actual* rate of diffusion out of the fibre is so low that it would take years to wash off the dye to any appreciable extent in water, although stripping agents like pyridine can speed up the rate of extraction. The levelling properties of a dye thus depend on the speed with which it diffuses *out*, while the fastness depends on the slowness of the outward diffusion; the speed of dyeing ("strike") and the depth of penetration depend on a high rate of diffusion *into* the fibre, but low rates of diffusion prevent unlevel dyeing. Each of these rates should be considered separately before dealing with their combined effect.

ACTIVATION

Let us consider dye molecules in solution in the dyebath. Some molecules have more energy than the rest— they are moving faster— and when they collide with the fibre they are able to penetrate and diffuse further into it. The molecules with lower energies do not have enough momentum to enable them to force their way in, and they bounce back and remain in solution. The rate of diffusion is thus determined not by the total concentration of dye molecules in solution, but by that fraction of the total which is in this "active" state of having high energy. To become "activated", a dye molecule may be moving at high speed or may momentarily have lost its sheath of hydrating water molecules, or it may have got itself disentangled from the attraction of the other dye molecules in an aggregated complex. How it has become activated need not concern us here— all we need consider is the fact that in some way it is at a higher free energy level than the rest*.

ACTIVATION ENERGY

Now the fibre, too, plays a part in all this, for it is the keratin which presents an energy barrier to the molecules and allows only those which have enough energy to get over the barrier. If we draw a picture of the barrier (Fig. 2), it looks like a switchback railway over which only those cars travelling fast enough can climb. Once over the hill, they can coast down easily, and this corresponds to diffusing into the depths of the fibre. The higher the barrier or "activation energy", as it is called, the slower the rate of diffusion, because there are then fewer molecules so fortunate as to have enough energy to diffuse into the fibre.

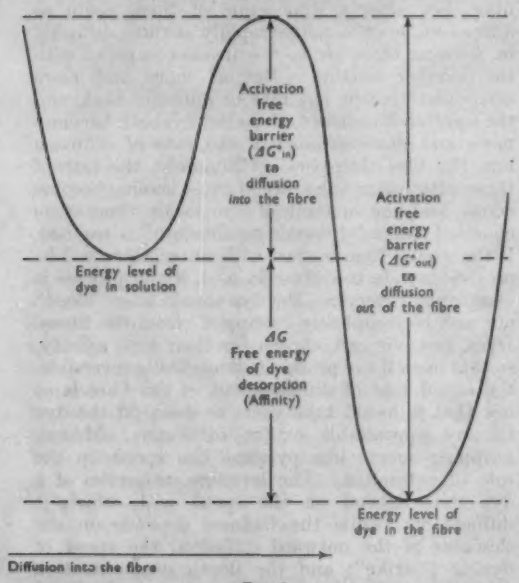
Activation free energy barrier ($\Delta G^{\ddagger}_{in}$) to diffusion into the fibre
Activation free energy barrier ($\Delta G^{\ddagger}_{out}$) to diffusion out of the fibre
Energy level of dye in solution
ΔG Free energy of dye desorption (Affinity)
Energy level of dye in the fibre
Diffusion into the fibre

FIG. 2

* By free energy is meant the energy which counts in determining the activity of the molecules— not energy which is locked up in vibration or rotation, which might influence the colour but not the rate of diffusion.

TEMPERATURE EFFECTS

It is not usually possible to lower the barrier to speed up the rate of diffusion, but by raising the temperature a bigger proportion of dye molecules can be given sufficient energy to overcome the barrier, and this has an equivalent effect. In fact, it is by measuring the speeding-up caused by raising the temperature that one estimates the height of this "activation energy"* barrier. When one says that the diffusion has a zero activation energy, one is merely saying that temperature has no effect on the speed of diffusion. A unit of activation energy could then be chosen to be that which increases the rate tenfold for each degree rise in temperature. Just as on the scale of affinities, this scale is logarithmic, and an activation energy of two such units indicates that the rate becomes another ten times as big (i.e. $10 \times 10 = 100$ times as big as at the first temperature), while three units would mean it goes 1,000 times as rapidly per degree rise, and so on. Such enormous sensitivity to temperature hardly ever occurs in practice, and a much smaller unit is more convenient, i.e. one which corresponds, say, to a twofold increase in speed due to a 10°C. increase in temperature. If the initial temperature is 90°C. (194°F.) such a unit can be expressed as 18·8 kilocalories per mole. Consequently, an activation energy barrier of $2 \times 18{\cdot}8 = 37{\cdot}6$ kilocal./mole is one for which the rate increases fourfold for a 10°C. rise in temperature, while one of $3 \times 18{\cdot}8 = 56{\cdot}4$ kilocal./mole is such that if the dyebath is 10°C. hotter, diffusion would be eight times as rapid; and so on, the rate being doubled each time. On this scale an activation energy of 62 kilocal./mole means that a 10°C. rise in temperature at 90°C. would make the rate of diffusion ten times as rapid. The effect of temperature for any other given activation energy can thus be found by dividing it by 62 and looking up the answer in antilogarithm tables. Suppose a figure of 10·9 kilocal./mole is quoted as an activation energy. Dividing this by 62 gives 0·176, and in antilogarithm tables this corresponds to 1·5. A rise in temperature of 10°C. for a dye of such an activation energy thus causes the rate to be $1\frac{1}{2}$ times as fast, and the time of half dyeing to be reduced to $\frac{2}{3}$ of what it was.

In the above calculations the initial temperature was assumed to be 90°C., since this is fairly likely to be close to the temperature used in wool dyeing. A 10°C. increase at other temperatures would not, of course, be in the same proportion, and the unit of 62 kilocal./mole (given above) must be different at other temperatures. At 0°C., for instance, it is found to be 34; at 20°C. it is 40; and at 80°C. it is 58. A simple rapid rule for working out its approximate value at any given temperature is to add 34 to three-tenths of the temperature in degrees centigrade. But these calculations can be avoided by the use of Fig. 3. At any required temperature, the corresponding increase in the rate of diffusion (or the rate of any chemical reaction, for that matter) caused by a 10°C. rise in temperature can be read off for any given activation energy value.

* The term "activation *energy*" is not strictly correct. It should be called heat of activation.

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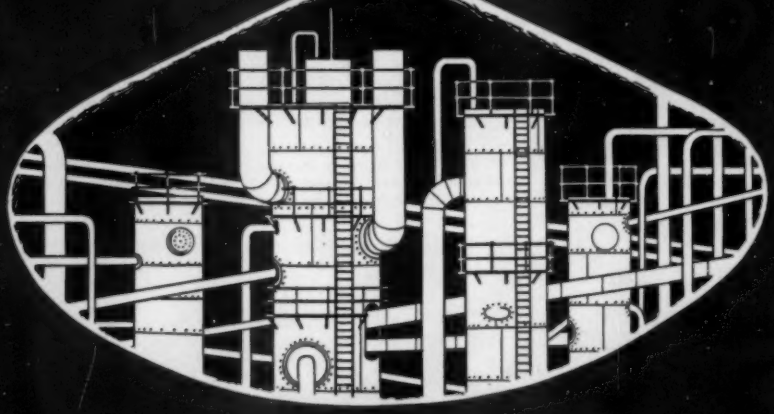

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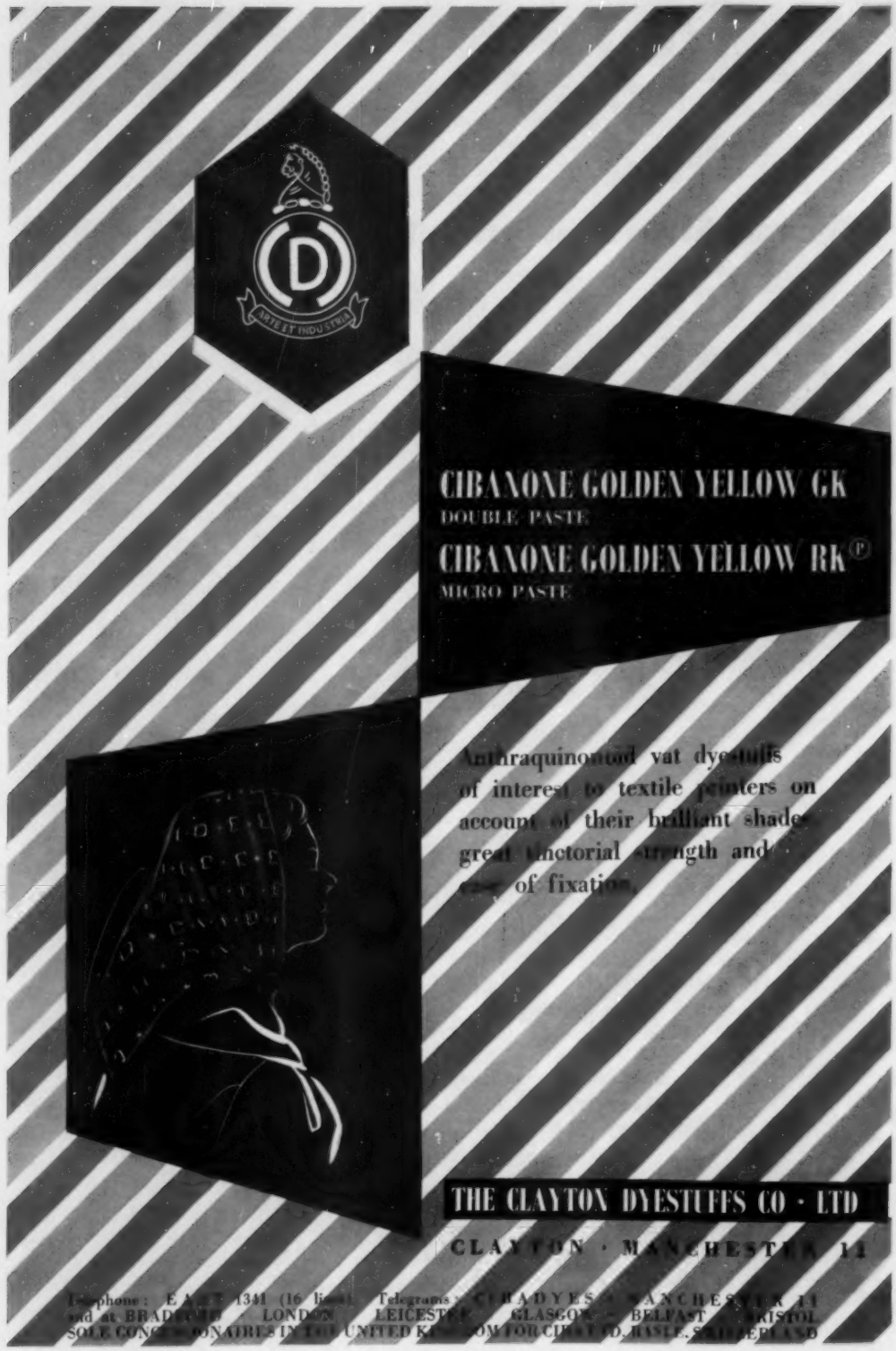
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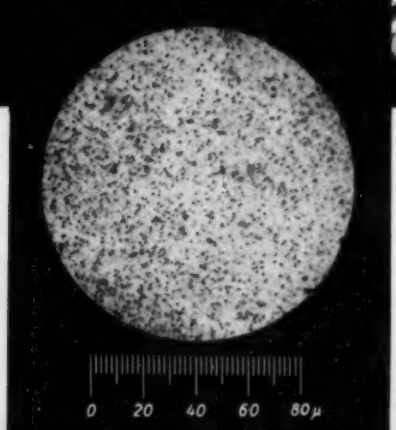

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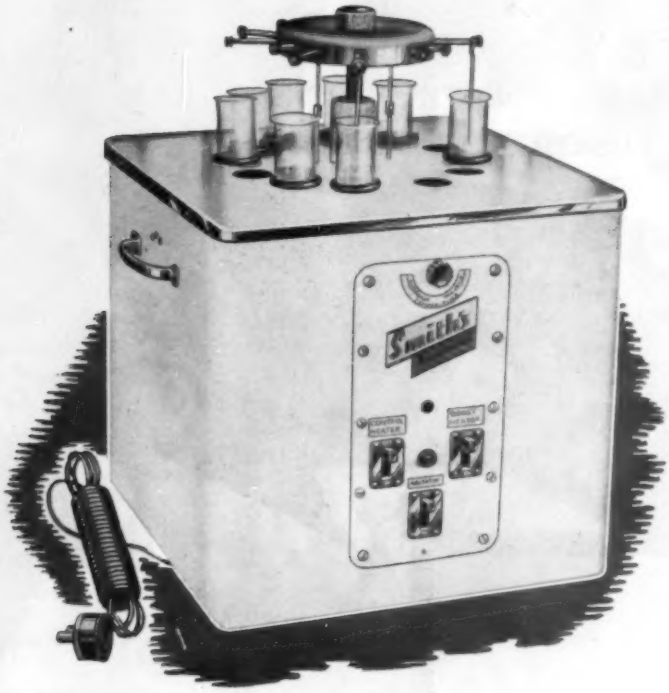

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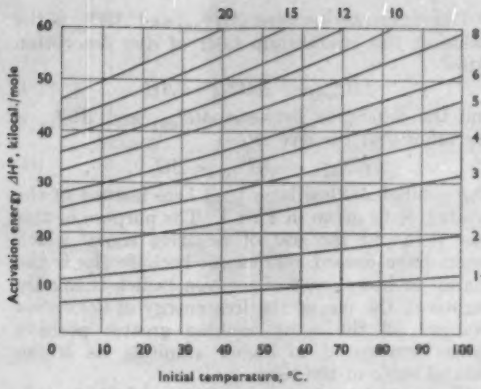


The figures at the ends of the curves are the factors by which the rate of the process is increased by a 10°C. rise in temperature

FIG. 3

For instance, from the graph it can be seen that at 50°C. an activation energy of 30 kilocal./mole corresponds to dyeing becoming just over four times as rapid when the temperature is raised to 60°C. But raising it from 60° to 70°C. will make the process only about $3\frac{1}{2}$ times as rapid. Altogether, however, the change from 50° to 70°C. will have made the rate $4 \times 3\frac{1}{2} = 14$ times as great.

MORE ABOUT EQUILIBRIUM

All that has been said about the rate of diffusion into the fibre holds equally for diffusion out of the fibre. If the activation energy barrier ΔH^*_{out} preventing dye molecules escaping is the same as that preventing them from penetrating ΔH^*_{in} (as shown in Fig. 4*a* and 5*a*), a rise in temperature will cause an equal increase in the rates of diffusion both into and out of the fibre, and the equilibrium state will, in this case, be unaffected by the change of temperature. When this is so, the equilibrium heat of dye desorption ΔH is zero; i.e. the dye combines with the fibre without heat being given out or taken in, a fact which indicates that the dye itself has little affinity for keratin*. But when the barrier to outward diffusion is much bigger than that for inward diffusion (as shown by the diagrams in Fig. 2 and 6) the outward rate is much more temperature-sensitive than the inward rate. Increase of temperature then makes the dye diffuse out more rapidly but does not affect the inward rate so much, and the equilibrium state is disturbed in such a way that less dye is absorbed. In this event, the heat of dye desorption is positive ($\Delta H > 0$), for heat is *given out* on combination, corresponding to a high intrinsic affinity between the dye and the protein. On the other hand, negative heats of dyeing ($\Delta H < 0$) mean that increase in temperature causes more dye to go on to the fibre; i.e. *less* is desorbed. Negative heats of dyeing are rarely met with, positive values of ΔH being the most common; i.e. increase of temperature usually speeds up the reaction and increases levelling by reducing the affinity—the main reasons for dyeing at the boil.

ENTROPY OF DYEING

The free energy change ΔG when a dye leaves the fibre (a measure of the affinity of the dye) is not just the heat change ΔH but is made up of two parts, according to the equation—

$$\Delta G = \Delta H - T\Delta S \qquad \text{(vii)}$$

where T is the absolute temperature ($273 + t$°C.) and ΔS is the gain in entropy which occurs on desorption. It is this last property (entropy) about which most people, even many physical chemists, find difficulty in forming a clear concept.

In order to see what these terms mean, it is perhaps useful to invent a mechanical analogy of the chemical process of dyeing so that what is going on can be more easily visualised. In place of the fibre absorbing coloured ions from solution, imagine an endless belt possessing small pockets or sockets in its surface. It is rotating constantly and dips into a tank containing steel ball-bearings, which it dredges up into the pockets. The pockets on the belt represent sites for dye absorption by the fibre and the ball-bearings represent the coloured dye ions. At the bottom of each pocket must be imagined an electromagnet which can be made to vary its attraction for the steel ball-bearings. When the magnets are switched off, only half of the pockets will be occupied, i.e. those in the upper half of the belt, and this corresponds to zero affinity. As the magnetic force is increased the fraction of occupied sites increases, as would occur for greater values of ΔH in dyeing, corresponding to greater affinity*. The strength of the magnetic attraction can be measured by rotating the belt more rapidly until the speed throws off some of the ball-bearings, and this is similar to the way in which ΔH is estimated from the amount of dye desorbed by increase of temperature, the speed of the belt corresponding to the temperature. The strength of the bond formed between the dye and the substrate is thus measured by the value of ΔH. But we must now consider what the term ΔS represents. As the negative sign in equation (vii) shows, its usual influence is to make ΔG smaller. The previous mechanical model can exhibit an effect similar to entropy if pennies are used instead of ball bearings. If the sockets are just the right size for pennies, it is improbable that by chance each penny will fall snugly into a socket, and because of this improbability the number of occupied sockets is reduced. Entropy acts similarly in dyeing in some cases, but in others ΔS is negative and *decreases* the affinity*. In wool, for example, entropy is the major contributor to the affinity. How can this be? In the mechanical model, if at the bottom of the sockets there are slots and the pennies fall through the slots into a cavity (like a money-box), the improbability of the coins orienting themselves properly to get out prevents them from easily escaping. In a similar way a dye may diffuse into the material but, once inside, undergo a change in shape so that it becomes almost impossible for it to diffuse out again. In this way very high affinity can be achieved.

* *N.B.*—This is not the only factor influencing affinity.

ENTROPY OF ACTIVATION

The activation free energy barrier to inward diffusion ΔG^*_{in} also includes an entropy term ΔS^*_{in} not measurable by changing the temperature. This entropy term expresses the probability of a dye molecule having the correct orientation necessary to penetrate the fibre, even if it has a high enough velocity or energy. When molecules with sufficient momentum (or satisfying the other conditions for being activated) penetrate at every collision, there is said to be a zero entropy of activation. If, of all the possible ways the dye molecule can be oriented, only one-tenth are effective in permitting diffusion, a unit of activation entropy is postulated, and this unit is given the value of 4·6 cal./mole per degree centigrade to make it agree with the units chosen for affinity*. For a dye whose large size and complicated structure make penetration impossible in all except one-hundredth of the possible ways of colliding, two units of activation entropy of 9·2 cal./mole per degree are assigned to it; one-thousandth would correspond to three units, i.e. $3 \times 4{\cdot}6 = 13{\cdot}8$ cal./mole per degree, and so on, in the same sort of logarithmic scale as before.

A similar activation entropy of diffusion out of the fibres ΔS^*_{out} depends on the probability of a dye molecule having the correct orientation to be able to escape, like the pennies in the money-box. There can thus be a greater entropy barrier to escaping than to penetrating, and this is expressed by saying that there is a decrease in entropy of the system when the dye goes from the fibre into the dyebath ($\Delta S > 0$). Another way of looking at this situation (for it occurs in dyeing wool, particularly at high temperatures) is to regard the dye, keratin, and water as a system which has more degrees of freedom (ways of possessing energy) when the dye is in the keratin than when it is dissolved in the water outside the fibre. This seems a little unbelievable until it is recalled that dyeing is accompanied by the liberation of water molecules previously held in a well oriented form around the charged groups of the keratin. It is these water molecules which have gained more freedom than the dye molecules have lost—there being an overall gain in freedom by many water molecules being displaced by one large dye molecule. The dye goes in (and stays in) because such a gain in freedom leads to a more probable equilibrium state—it is very unlikely for all the water molecules to return spontaneously and take up their previous orientation—and this is expressed by saying that the probability of desorption is small, i.e. the entropy of desorption ΔS (a logarithmic function of the probability) is negative.

HOW TO INTERPRET ACTIVATION BARRIERS

As shown above, there are four thermodynamic parameters which characterise the rate of diffusion of a dye: ΔH^*_{in}, ΔS^*_{in}, ΔH^*_{out}, and ΔS^*_{out}. At any given temperature T, ΔG^*_{in} or ΔG^*_{out} can be calculated from these four by using equations of the form of (vii), so that it is only necessary to know the ΔH and ΔG values to get a picture of the dyeing process.

The difference between ΔH^*_{out} and ΔH^*_{in} is the value of the equilibrium heat of dye desorption ΔH—

$$\Delta H^*_{out} - \Delta H^*_{in} = \Delta H \qquad \text{(viii)}$$

and the difference between ΔG^*_{out} and ΔG^*_{in} is the affinity of the dye ΔG—

$$\Delta G^*_{out} - \Delta G^*_{in} = \Delta G \qquad \text{(ix)}$$

The symbol ΔG has been used here instead of the symbol $-\Delta\mu$ given in Part I. The purpose of this was to avoid the use of negative signs, which might have caused confusion. Because $\Delta\mu$ is the change in free energy of *sorption* (which is usually negative), the use of the free energy of *desorption* changed all the signs, making greater positive values correspond to higher affinities, as is the natural sense of the term.

Fig. 4–6 give a convenient way of illustrating the sort of dyeing properties characterised by various combinations of the four parameters. In each diagram, the energy state of the dye in solution is represented by the left-hand level and that of the dye in the fibre by the right-hand level. The left-hand side is never shown lower than the right-hand side, because dyeing is concerned only with dyes of high affinity. If other possibilities are required, the same graphs may be used with the reverse interpretation.

The six possible types of G curves (with the above limitation) are shown in the diagrams, but there are ten possible H curves, because there need be no such limitation where ΔH is concerned so long as the ΔS term is negative and sufficiently large to confer affinity on the dye. By choosing one curve of each type, sixty different types of behaviour can thus be described.

Take, for example, a dye which has an H curve of the form shown in Fig. 4(a) but with a G curve as in Fig. 6(a). Such a dye will rush on rapidly, and therefore dye unlevel, because ΔG^*_{in} is small, but it will not level itself easily because the barrier ΔG^*_{out} to redistribution is so large. Prolonged boiling will not help levelling, since the barrier to diffusion out of the fibre is not a ΔH term (which would indicate that the rate is affected by temperature) but is an entropy effect.

Consequently, it is vain to search for a dye which will go on rapidly, with high affinity, and also be a good levelling dye, for such properties are mutually contradictory. A dye which goes on slowly, however, can go on level and still have a high affinity, e.g. one with a G curve like that of Fig. 2. Provided that its H curve is like Fig. 5(a), higher temperatures can be used to speed up the rate if required, without altering the affinity, i.e. the degree of exhaustion of the dyebath. One with an H curve like Fig. 2, but reversed, can be made to level itself by increase of temperature only at the expense of reducing the exhaustion.

What will occur with any other combination of curves should now be easy to deduce in a similar way.

WHAT IS THE USE OF DYEING THEORY?

The practical dyer may now well ask: "What use is all this theory to me?"; and it must be confessed

* $4{\cdot}6 = R \ln 10$ where $\ln 10 = 2{\cdot}303$ and $R = 1{\cdot}987$ cal./mole per °C.

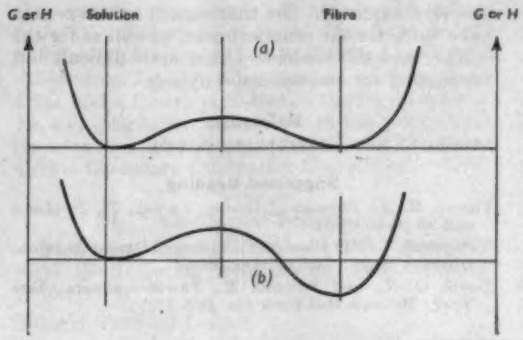


FIG. 4— Free Energy G Curves

(a) and (b) Rapid dyeing, good levelling, poor exhaustion
(a) Zero affinity
(b) Low affinity

FIG. 4— Heat Content H Curves

(a) and (b) Rates of diffusion only slightly affected by change in temperature
(a) Equilibrium (exhaustion) unaffected by change in temperature
(b) Equilibrium (exhaustion) only slightly affected by change in temperature

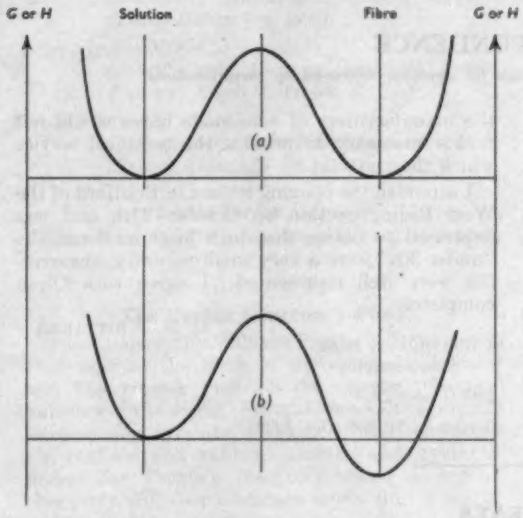


FIG. 5— Free Energy G Curves

(a) and (b) Slow dyeing, poor levelling, poor exhaustion
(a) Zero affinity
(b) Low affinity

FIG. 5— Heat Content H Curves

(a) and (b) Rates of diffusion (both inward and outward) greatly affected by change in temperature
(a) Equilibrium (exhaustion) unaffected by change in temperature
(b) Equilibrium (exhaustion) only slightly affected by change in temperature

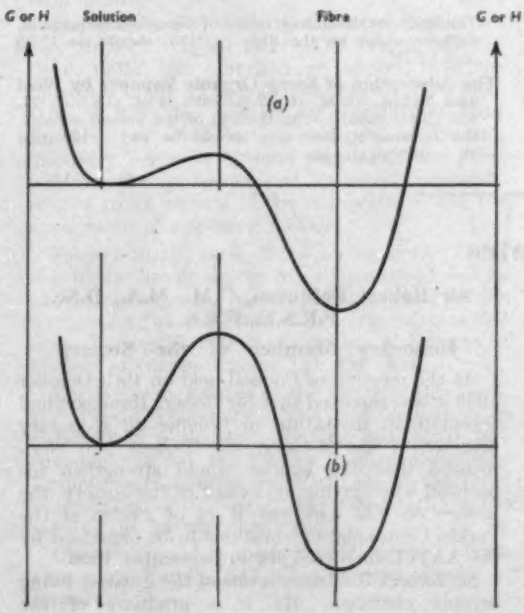


FIG. 6— Free Energy G Curves

(a) and (b) Poor levelling, high affinity, good exhaustion
(a) Rapid, unlevel dyeing
(b) Slow, level dyeing

FIG. 6— Heat Content H Curves

(a) and (b) Equilibrium (exhaustion) very sensitive to change in temperature
Rate of outward diffusion increased by rise in temperature
(a) Rate of inward diffusion not very sensitive to change in temperature
(b) Rate of inward diffusion very sensitive to change in temperature

FIG. 4–6— Typical G and H Curves for Dyes of Various Dyeing Characteristics (six types of G curve combined with six types of H curve give thirty-six possible combinations of dyeing properties).

All the examples have been chosen to show zero or positive affinity ($\Delta G > 0$). Similarly, only zero or positive values of ΔH are shown, i.e. for dyeing systems in which increase in temperature either has no effect or brings the dye *off* the fibre. (Cf. Fig. 2.)

that it is not directly of much value to him. Over the past few decades, with many sorts of fibres and many more dyes, the dyer has accumulated a wealth of experience which is now largely intuitive. Dyeing theory attempts to make such knowledge conscious, and to unify it into simple concepts which can thus be learnt by the beginner more quickly than by the slow method of trial and error of the past. In this way, the theorist plays the part of the mapmaker, following in the footsteps of the pioneering explorer of new processes. But even explorers find maps interesting and, sometimes, useful. Maps may suggest short cuts not obvious from the ground, or territory not yet properly explored. To that extent, theory may have value for the practical man, as well as for the teacher and the student of that most difficult but fascinating art and science— dyeing.

Reference

[1] Peters, L., J.S.D.C., **71**, 174 (April 1955).

Suggested Reading

Turner, H. A., *Theories of Dyeing*, J.S.D.C., **71**, 29 (Jan.) and 96 (Feb. 1955).

Vickerstaff, T., *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954).

Lewis, G. N., and Randall, M., *Thermodynamics* (New York: McGraw-Hill Book Co. Inc. 1923).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Theories of Dyeing

May I briefly reply to Dr. L. Peters[1] and Mr. H. C. Olpin[1] that both avoid answering my simple question as to the standards of knowledge required to understand the Explanatory Papers on Modern Dyeing Theory. The amusing quip about common sense always awaits me, but is not an answer.

It is axiomatic to say that a first-class technologist is a first-class scientist. Anyone who has had similar technical service experience to myself must be aware that many of those responsible for processing the material in dyehouses would not be classed as understanding the papers on which I commented. If they were, surely the dyemakers and the manufacturers of man-made fibres would not find it necessary to provide the technical service which they now do.

I attended the opening lecture in Bradford of the West Riding Section on October 27th and was depressed to notice that in a large audience the "under 30s" were a very small minority; the over-50s were well represented. I agree with Olpin completely.

C. M. Whittaker

1 Weaponness Park
Scarborough

29th October 1955

[1] J.S.D.C., **71**, 609 (Oct. 1955).

ERRATA

Coal-tar Colours— XVII, by R. N. Solar and K. A. Freeman (J.S.D.C., **71**, 70 (Jan. 1955))— The dye should be Ext. D&C Red No. 11 and the page number should be 913.

The Affinities of Vat Dyes in Relation to their Constitution, by R. H. Peters and H. H. Sumner (J.S.D.C., **71**, 137–138 (March 1955))— In the Appendix the concentration units of $[Na]_f$ are gram-ions per litre (**not** $\times 10^3$).

The figure for the concentration of 1-amino-5-benzamidoanthraquinone on the fibre (p. 138) should be 17·23 (not 12·23).

The Adsorption of Some Organic Vapours by Wool and Nylon, by H. R. Chipalkatti *et al.* (J.S.D.C., **71**, 658 (Nov. 1955))— At the top of the second column, the internal surface area should be 40×10^5 (**not** 40×10^7) sq.cm. per gram.

Notes

Meetings of Council and Committees
November

Council— 9th
Finance and General Purposes— 9th and 14th
Publications— 15th
Diplomas— 2nd
Diplomas Examinations Board— 2nd
Colour Index Editorial Panel— 14th
Perkin— 10th
Perkin Executive— 25th
Perkin Publicity— 22nd
Textbooks and Monographs Subcommittee— 15th

Sir Robert Robinson, O.M., M.A., D.Sc., F.R.S.E., F.R.S.
Honorary Member of the Society

At the meeting of Council held on 19th October 1955 it was reported that Sir Robert Robinson had accepted an invitation to become an Honorary Member of the Society. Sir Robert had commented that the honour would strengthen his position when giving, on behalf of the Society, the lecture on *The Life and Work of Perkin* at the Perkin Centennial Celebrations to be organised by the AATCC in New York in September 1956.

Sir Robert Robinson is one of the greatest living organic chemists. He is a graduate of the

University of Manchester and has recently retired from the Waynflete Chair of Chemistry in the University of Oxford. He is President of the British Association for the Advancement of Science for 1955, and a former president of the Royal Society. He has long taken an interest in the work of the Society, and is at present Chairman of the (joint) Perkin Centenary Celebration Committee.

Election of Fellows

At the meeting of Council held on 9th November 1955 the following were elected Fellows of the Society—

Ronald Strafford Ledger
(*Stockport; Assistant Chemist, English Sewing Cotton Co. Ltd.*)

Edgar Irvine Noble
(*South Yarra, Victoria, Australia; Senior Partner, Edgar I. Noble & Co.*)

Walter Taussig
(*Manchester; Technical Representative, Clayton Dyestuffs Co. Ltd.*)

Leeds Junior Branch

Mrs. Joan M. Firth has been elected Honorary Secretary.

The Perkin Centenary Fund

The discovery by William Perkin of Mauveine in 1856 marked the birth of the dyestuffs industry and the greater part of the organic chemical industry of the world. From these small beginnings have sprung dyes and pharmaceuticals, chemicals for textiles and rubber, plastics and synthetic fibres; for Perkin's discovery changed organic chemistry from an academic study into a world-wide industry.

The Perkin Centenary Celebration Committee (see J.S.D.C., **71**, 610–611 (Oct.) and 667–668 (Nov. 1955)) has launched an appeal, over the signature of its Chairman, Sir Robert Robinson, O.M., F.R.S., for support for a £100,000 Trust Fund to provide a lasting memorial to Perkin's discovery. A more specific purpose of the Fund will be the promotion of technical education related to all aspects of the manufacture and the application of colouring matters.

Subject to approval of the terms of the Trust, it is likely that donations made by a trader will be allowed as expenses in computing trading profits for Income Tax and Profits Tax purposes, provided that the donation is made within the terms of Section 140 of the Income Tax Act 1952.

Furthermore, subject to the terms of the Trust, the Perkin Centenary Fund will probably be regarded as a charity. Thus an individual who covenants to pay the Fund a fixed sum annually for not less than seven years will enable the Fund in addition to recover income tax which he has paid at the full standard rate.

Cheques should be made payable to the "Perkin Centenary Fund", and all payments should be forwarded to—

The Perkin Centenary Fund
Martins Bank Ltd.
Queens Park Branch
476 Rochdale Road
MANCHESTER 9

In order that the target of £100,000 may be reached it is hoped that both firms and individuals will contribute generously to this Fund, the purpose of which is so closely related to the objects of the Society.

Exhibition of English Printed Textiles Manchester, 13th December 1955 to 31st January 1956

The exhibition is being presented by the Cotton Board Design Centre, the research and the selection of material having been the responsibility of Mr. Peter Floud, C.B.E., Keeper of the Circulation Department of the Victoria and Albert Museum, London S.W.7.

The exhibition was originally planned with the deliberate aim of arousing interest in a subject that has hitherto received very little systematic attention or study— namely, the history of English printed textiles. Whereas many exhibitions and books have been devoted to their French counterparts, no comprehensive exhibition of English printed textiles has ever been held, no serious study of them has ever been published, and, with the exception of the Victoria and Albert Museum, no public museum in England possesses even a single interesting example of English chintz.

The original plan involved no more than the collection and exhibition of those relics of English calico-printing which seemed of particular interest or beauty. However, thanks to the readiness with which the many organisations approached were prepared to allow free access to their archives, it soon became clear that the search for documentary records and surviving textiles would prove far more fruitful than had been anticipated. It consequently became possible to envisage a much more ambitious project— namely, a systematic visual survey of English printed furnishing textiles almost year by year over the greater part of the last two centuries. This is what has now been attempted.

The word *chintz* has been used in the exhibition not in the limited sense of a highly glazed floral fabric but as a convenient term to cover all printed furnishing fabrics. Examples of Irish and Scottish printing have been excluded not because they lack interest but because it has so far proved impossible to discover enough records and samples to enable their history to be reconstructed.

Among hitherto unpublished sources of information employed in compiling the catalogue are pattern books covering the years 1760–1840, the Patent Office Design Register (1842–1910), and William Morris's dyeing records (1875–1890). The pattern books prove that many textiles, previously thought to be French, are English.

The exhibition shows that the leading English designers of each decade since the eighteenth century have introduced new and original designs and styles, so that it is misleading to speak of a single "traditional" English chintz style.

The Society of Dyers and Colourists of Australia

ANNUAL REPORT 1954–1955

The Council has pleasure in presenting its seventh Annual Report. It is very gratifying to note from the reports from the honorary secretaries that all sections show increased activity and progress during the year ending 31st May 1955.

COUNCIL— The Council met on 15th July 1954 in Sydney, and in the absence of the President, Mr. W. C. Castle, the Immediate Past President was elected Chairman.

Mr. G. Athol Burns was elected President by the Council.

The resignation of Mr. R. L. Runting as Editor was accepted with regret, and Mr. D. L. Turner was appointed in his stead. The Honorary General Secretary and the Honorary General Treasurer were re-appointed; the Auditors were also re-appointed.

The Council approved the formation of a new Section in Western Australia, and the formation of a Geelong Subsection of the Victorian Section. The Council ruled that the Geelong applicants should become Country Members of the Victorian Section. These members could then be formed into a Subsection, and conduct their own affairs, but they would be at all times members of the Victorian Section.

The Council agreed to recommend to the Sections that the Annual General Meeting of the Society should be held in August instead of June, at the Sectional Meetings, as requested by the Victorian Section. This proposal has met with the approval of the majority of the members.

FINANCES— The Balance Sheet was adopted by the Council. The Honorary General Treasurer reported that all Sections were sound financially and that the total assets of the Society were £A909 12s. 1d. He drew attention to the large cash balances held by the Sections, which were contrary to Rule 47, paragraph 2, in the Bye-laws, and the Councillors agreed to request their Sections to conform, so that the Society would be strengthened.

MEMBERSHIP— Total membership has increased during the year by 96 members. The present membership is shown in the list with the previous year's figures in brackets.

	Life	*Full*	*Country*	*Junior*	*Total*
Victoria	3	175	53	6	237 (213)
New South Wales ...	1	97	4	—	102 (92)
South Australia ...	—	32	—	—	32 —
Queensland ...	—	33	—	—	33 (24)
Western Australia ...	—	21	—	—	21 —
				Total ...	425 (329)

The Council decided that overseas members in New Zealand or in other countries should be considered Country Members of the Victorian Section, and that applications for membership should be made to that Section.

MEETINGS— Generally, meetings were well attended, especially in Victoria, where the average attendance has risen from 46 to 55 members. The Victorian Section is to be congratulated on making its meetings and subjects so interesting.

Victoria— Eight lecture meetings have been held. A week-end convention was held at Clifton Springs and a Film Night was enjoyed with the Geelong Textile Society. Members attended a Film Night held by the Australian Textile Society. Over 100 members and guests attended the Annual Dinner on 29th April 1955. The Annual Ball was held on 22nd October 1954 and was very successful.

New South Wales— Nine lectures have been given. The Annual Dinner was held in October and was very successful, 52 members being present. During the year the attendance at meetings has increased about 50% compared with the previous year. Several important executives in N.S.W. dyeing circles have now joined the Society, adding prestige to the Section, and the officers of the N.S.W. Section were pleased with the increased interest being shown by members. Careful choice of suitable lectures has been an important factor in achieving this progress.

South Australia— Meetings have included four lectures, two groups of three or four short lectures, a film night, a general discussion, a works visit, and the Annual Dinner. The average attendance at these functions has been about 60% of the total membership, a high tribute to the enthusiasm of the members of the S.A. Section. Prior to each meeting members have dinner together in the South Australian Railways' Private Dining Room, a most enjoyable feature of their meetings. Other sections are not so fortunate in being able to obtain meals at such nominal charges for excellent food and wines, but should the possibility arise, this procedure to attract the attendance of members is recommended.

Queensland— Eight lectures have been given in this Section. A successful film evening was held in December, which was well attended, and a Christmas Party was also held, which was a great success.

Western Australia— More than six lectures have been given in this Section. A film night was well attended and much enjoyed.

Our President, Mr. G. Athol Burns, has visited the Western Australian and Queensland Sections, and has regularly visited the New South Wales Section. To these Sections he has given his Presidential Address, entitled *Commission Dyeing*, and this will be given to the other Sections soon. Our President plans to go to England this year and represent our Society at meetings of the Society of Dyers and Colourists in Great Britain.

The President's Golf Trophy was contested by members of the Victorian, N.S.W., and Queensland Sections. Mr. J. Everett, Immediate Past Chairman of the Queensland Section, again won the Trophy for the best net score against par.

Our Editor, Mr. D. L. Turner, has maintained the high standard of publications in the *Textile Journal of Australia*, and the assistance of Mrs. A. Mardell, the Editress, is again appreciated.

We are indebted to the authors of lectures and papers for their hard work for the Society and for permitting publication.

Your Council wishes to express to all members who have given their time in serving the Society its gratitude for the excellent work done. The Council is particularly pleased to note the increased activities of some of the younger members of the Society in working for it.

E. I. NOBLE
Honorary General Secretary

Proposed International Commission on Fastness Properties of Leather Dyes and Dyed Leather

The Swiss Society of Leather Trades' Chemists formed a Committee in 1952 for the study of methods for the testing of leather dyes and dyed leather. On the basis of work already carried out by the Swiss dyemaking industry, the textile industry, and the S.D.C. Fastness Tests Committee, the Swiss Committee decided after extensive experimental work to examine the following—

(1) Solubility of leather dyes
(2) Acid fastness of leather dyes
(3) Alkali fastness of leather dyes
(4) Uptake of dyes
(5) Resistance of leather dyes to fat-liquoring
(6) Light fastness of dyes and dyed leather.

For comparison of differences in colour (e.g. dyed leather before and after fat-liquoring), a grey scale is used, which has already been introduced for the testing of textile dyes.

The method of measuring light fastness is essentially the same as for textiles, using the international blue scale.

For the examination of the resistance of leather dyes to fat-liquoring, or for assessing light fastness, a standard chrome leather has been developed that guarantees the reproducibility of the results.

In view of what has been accomplished by the above Committee, collaboration with similar committees in other countries is desirable, so that existing methods can be studied and unified.

At the recent Stockholm Conference of the International Union of Leather Chemists Societies it was decided to form an International Commission on the matter, and with this end in view interested parties should communicate with Dr. W. Weber, Swiss Federal Testing Station, St. Gallen, Switzerland.

Titanium Pigments to be made in Canada

The first Canadian plant for the manufacture of titanium pigments is to be built near Varennes, Quebec, by Canadian Titanium Pigments Ltd.

C. O. C.

Paint Testing Laboratory at the Borough Polytechnic, London

In September Lord McCorquodale opened the new Paint Testing Laboratory at the Borough Polytechnic, London, and presented to the chairman of the Governors testing equipment purchased from funds subscribed by industry, through a committee consisting of representatives of the Society of British Paint Manufacturers, the London Colour, Paint, and Varnish Manufacturers' Association, and the London Sections of the Paint Manufacturers and Allied Trades Association and the Oil and Colour Chemists' Association. The testing equipment installed is similar to that used extensively in government and other laboratories for the examination of the properties of paints, e.g. resistance to humidity and other atmospheric conditions. The Borough Polytechnic, which is one of the twenty-five institutions in England and Wales recognised by the Ministry of Education as senior colleges of technology, has for sixty years provided courses in paint technology.

OBITUARY NOTICE

Herbert Bradley Briggs

It is with great regret that we learned of the death of Herbert Bradley Briggs at the age of 58 on May 14th of this year. Whilst he did not take an active part in the affairs of the Society, Herbert Briggs had been a member for many years, having joined in 1919. He received his technical education at the University, Leeds, in the Department of Colour Chemistry and Dyeing, and his first post was with the Calico Printers Association Ltd., with whom he worked until 1930, when he was Chemist at their Reddish Vale branch. He then left them to take charge of the printing section of the Dyehouse Department of Imperial Chemical Industries Ltd.

Up to 1945 I.C.I. had the benefit of his long experience as a practical printer, but at that date a serious breakdown in his health necessitated a transfer to less exacting duties. During the years 1945–1950 Herbert Briggs took an increasing interest in the further education of the junior members of the staff of the Dyehouse Department, which led eventually to the formation of a special section which became responsible for the preliminary training of new recruits to the company and also the many people from the dye-using industries who came to the laboratories of I.C.I., not only to gain knowledge of the specific products of the company but also to obtain a general training in dye technology.

Whilst Herbert Briggs's interest in technical education was confined within the commercial ambit of I.C.I., there was no question that he was making a useful contribution to the dissemination of knowledge concerning the technology of the application of dyes, and there will be many people both at home and abroad who would be the first to acknowledge their indebtedness to Herbert Briggs for a thorough grounding in the basic principles of textile technology. There was much in his character which reminded one of the benevolent schoolmaster who could temper the austerity of tuition with typical Yorkshire wit.

We mourn the passage of one who has made his contribution to the furtherance of technical education, and we convey to his widow and his daughter our very deepest sympathy in their loss, which was made all the greater by the suddenness with which it occurred. H. BLACKSHAW

New Books and Publications

The Structural Chemistry of Proteins

By H. D. Springall. Pp. x + 376 with 115 Fig. and 23 Tables. London: Butterworths Scientific Publications. 1954. Price, 45s. 0d.

Scientific monographs may be encyclopaedic or of current interest. The former, if up to date, must be written in the lulls of progress; the latter in the exciting tempo and hurly-burly of quick and fluctuating advances. Both have their points; but the English mind inclines to the latter with its brevity and utility, its clarifying and current stimulus, its broad focus, its emphasis on intelligent selection and critical insight rather than on exhaustive information.

The present volume, introduced by L. Pauling and compiled by essentially an organic chemist, is one such. Based on an Honours Course at Manchester University, it gives in five comparatively brief chapters an excellent conspectus, compact, objective, trebly distilled, of modern protein analytical and physical chemistry.

Following a brief introductory chapter on the classification, properties, and biological importance of these premier of the biological trinity of macromolecules with their peptide chain structure and hydrolytic degradation to natural α-amino acids, a classified survey is made of organic methods of peptide synthesis. The structural and physical chemistry of proteins occupies two solid chapters devoted to fibrous and globular types, respectively, an arrangement which, if overemphasising a distinction, is practical, clear, and in historical order. In the former chapter, the techniques are mainly X-ray, electron-microscopic, and infrared, the structural groupings following Astbury's classification. While essential facts and developments are given, and full weight is accorded the transfiguring contributions of the Pasadena, M.I.T., and Maidenhead centres, this is, perhaps, the least commanding chapter, necessarily suffering by timing before the Royal Society and Pasadena Conferences and without access to, for example, Low's summary in "Neurath–Bailey", or to the remarkable cognate advances of the King's College team. There are few minor slips, though these include an uncritical endorsement of curious Cambridge claims to "a new X-ray approach" in methods of not even local novelty. Conversely, in Chapter 4, it could be further stressed that the importance to date of the X-ray attack on globular proteins is rather one of powerful technical and methodological advance than of any new permanent detailed structure results. The methods cited are extremely comprehensive (osmotic pressure, X-rays including low-angle diffuse scattering, electron microscopy, electrophoresis, sedimentation equilibrium and diffusion, light scattering, viscosity, streaming double refraction, infrared absorption, dielectric constant, etc.), covering most macromolecular techniques whether towards isolation, purity criteria, or molecular structure and characteristics. Together with Chapter 4, the highlight of the book is undoubtedly the final (and longest) chapter, in which a comprehensive classification and appraisal of chemico-analytical methods and results is beautifully detailed. Features here are the graphical diagrams following procedure through all its stages, and the up-to-date tables of results including interconversion from different conventions.

Some 850 admirably chosen references concentrate on amplifying review-type papers, though key classics are carefully noted also. In addition to author and subject indexes, a welcome introduction is an index to "named" proteins and peptides.

This is an admirable text for the abler student, a good introduction for the research man, and a ready source for the harassed director seeking solid background. It would be difficult to add anything further without losing focus, and its general appeal should earn frequent revision. Style and format follow the distinctive Butterworth mode.

I. MACARTHUR

Moderne Wasch- und Reinigungsmittel

By H. Manneck. Garmisch-Partenkirchen: Moser-Verlag, F.E.B. Archiv.

This German publishing firm, the F.E.B. Archiv, aims at collecting the literature published in journals and publications on specific subjects and printing it as mimeographed monographs. These reports have now been published for seven years, providing industry with current information. The publication on *Modern Detergents and Washing Agents* is divided into seven parts, all written by Herr H. Manneck, who is a well known German

author and expert. He is a regular contributor to the German journal *Seifen, Öle, Fette, Wachse*.

Part I (30 pp. 1952. Price, DM 18), *Alkylsulfosäuren und -Sulfonate* (alkyl sulphonic acids and sulphonates), describes the methods of manufacture of these products and their application. It gives 178 references to German and foreign literature and patents. Supplement I/1 (48 pp. 1955. Price, DM 20) deals with further publications on this subject, particularly with the technique of sulpho-chlorination. There are 38 references to more recent literature, a list of German and foreign patents, and a list of trade names.

Part II (39 pp. 1952. Price, DM 15), *Waschen und Reinigen— Die Waschwirkung und ihre Prüfmethoden*, explains the chemical and physical principles of washing and laundering, the testing and evaluation methods for soap and synthetic detergents. To the list of references and books for further reading the work by W. W. Niven *Fundamentals of Detergency* (Reinhold Publishing Corpn. and Chapman & Hall. 1950) and *Detergency Evaluation and Testing* by J. C. Harris (Interscience Publishers. 1954) should be added.

Part III (33 pp. 1953. Price, DM 15), *Geformte Waschmittel* (detergents containing builders), was not submitted for review.

Part IV (56 pp. 1953. Price, DM 18), *Fettalkohole, Fettalkoholsulfate und Alkylsulfate*, surveys the raw materials and production methods for fatty alcohols, the manufacturing methods for fatty alcohol sulphonates and alkyl sulphates, and their industrial application. There are a list of trade names, and 59 literature and 230 German and foreign patent references.

Part V (62 pp. 1953. Price, DM 20), *Fettsäurekondensationsprodukte und nichtionogene Waschrohstoffe*, concerns fatty acid condensates and non-ionic washing agents. It is arranged in a similar manner to the other volumes, with trade names, references to literature and patents, and a table of the chemical composition of such products.

Part VI (50 pp. 1954. Price, DM 20), *Alkylaryl-Sulfosäuren und -Sulfonate*, deals with alkylarylsulphonic acids and -sulphonates; it is arranged as the other volumes, with a long list of trade names, and 45 literature and 183 patent references.

On the whole, all the volumes contain some useful information; one would have welcomed some more critical comment on the value of some of the manufacturing methods. One can compliment the author for his thorough and assiduous work in collecting all this material. The contents of some of the volumes are, in parts, more of historical than of practical interest. A. F. KERTESS

Principles of Emulsion Technology

By P. Becher. Pp. ix + 149. New York: Reinhold Publishing Corpn. 1955. Price, $3.00 or 24s. 0d.

The Reinhold Pilot Books series, to which this book belongs, is designed to present information on new materials, processes, or technologies in a short, concise form and in language understandable by the non-expert. This volume is intended for chemists desiring both theoretical and practical knowledge of emulsion technology.

Following a first chapter in which emulsions and allied systems are defined, a chapter on surface activity emphasises its importance, and discusses the phenomena resulting from such activity and the factors affecting them. This is followed by a discussion of the theory of emulsions which includes consideration of viscosity, phase volume, emulsion type, distribution of drop size, emulsion stability, and theories accounting for it. A chapter on the chemistry of emulsifying agents provides a useful summary of the many substances which may be used. Other topics include emulsification equipment, the testing of emulsion properties, and the formulation of emulsions. The choice of emulsifying agent, methods of emulsification, and different industrial emulsions are considered. There is a brief account of the breaking of emulsions.

Theoretical treatments are physicochemical but are very clearly explained. General principles are stressed, and their importance is illustrated by practical examples. In spite of the small size of this book, few important aspects seem to have been overlooked, although the Schulman–Cockbain theory of emulsion stabilisation might have been mentioned. Suggestions are made for further reading, and there are a few references to original work. The author has provided a very readable account, which will be of value to all interested in emulsions. W. R. MOORE

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Severe Pitting of Stainless (18-8) Steel in Hot Chloride Dyebaths. F. N. Speller. *Corrosion*, **11**, 303t (1955): *Chem. Abs.*, **49**, 11285 (25 Aug. 1955).

Severe pitting in welded and cast stainless steel dyeing equipment was highly localised at welds or in exposed porous spots in coatings. After several years the corrosion was so severe that the machinery had to be thoroughly cleaned every week to avoid rust stains on the fabrics and after 4 years many metal parts had to be replaced. The primary cause was fissures and cavities in poorly made welds which resulted in activation of the steel in the fissures, formation of passive–active cells, and some difference of potential. In similar equipment where the welds were smooth there was no local action at the welds. About 80% of the damage was obviated by adding about 500 p.p.m. $NaNO_3$ or Na_2CrO_4 to the dyebath before adding salt. A protective film was evidently built up which removed the chloride added in the later stages of dyeing. Thorough washing of the equipment after each lot of dye liquor has been run off is very important. C. O. C.

PATENTS

Drying and Currying Finely Divided Materials by means of a Hot Gas. H. Orth. *BP* 737,720

Wet-spinning Viscose Rayon. Courtaulds. *BP* 736,330

Apparatus is described for heating the acid liquors used in the regeneration of viscose so that the efficiency of the process is maintained. W. G. C.

Thread Treating Apparatus. H. A. Kuljian. *BP* 737,055

Improved liquid and segregating device of the type described in *BP* 686,026 (J.S.D.C., **69**, 125 (April 1953)). C. O. C.

Apparatus for Continuous Saponification of a Tow of Cellulose Acetate Filaments. Celanese Corpn. of America. *USP* 2,697,022

Spraying Liquid on to Textiles. Monsanto. *BP* 737,401

The liquid is picked up by a rotating wheel, cylinder or analogous device having a continuous surface and flung off by centrifugal force as a fine spray which is directed onto the textile material. The method is particularly suitable for applying silica sols which are liable to clog the jets of much spray equipment. C. O. C.

Yarn Setting. Alexander Smith. *USP* 2,695,509

Apparatus for yarn setting using steam, and if desired setting agents. The degree of set can be accurately controlled. C. O. C.

Travelling Supports for use in Hank Drying Machines. J. Dean. *BP* 735,853

Supports which move into different positions during their travel through the machine so as to shift the points of support of the hank and so expose the whole of the hank to the drying medium. C. O. C.

Expander Roll. J. D. Robertson. *BP* 736,674

If the central curvature of the roll is such that it gives correct expansion of the narrowest fabrics it may be required to treat, then the portions outward from this curvature may be straight and yet the roll will exert approximately the same stretching force on fabrics the width of its length as it does on the narrowest fabric. C. O. C.

Conveying Textile Fabric or other Material liable to Shrink or Stretch. Rydboholms AB. *BP* 735,341

The fabric passes in a zig-zag path around a series of rollers some of which are driven without slip by belts of rubber or other material which is more elastic than the fabric being printed. The belts are under tension and respond to variations in the tension in the fabric by complementary changes in their slack and taut sides. C. O. C.

Equalising the Tension on Webs having Baggy or Stretched Portions. Western Electric Co. *USP* 2,696,192

Apparatus for taking up the slack portions of a web as it passes over a coating roller. C. O. C.

Passing Webs through a Chamber. Benteler-Werke. *BP* 736,763

A definite length of the material is wound onto a roller in the chamber and then an unwound print of the material in the chamber is attached to a second roller which is then rotated so as to draw a double layer of the material onto it, one from outside the chamber and the other from the material already wound on the first roller. When the free end leaves the first roller, rotation of the second roller is stopped and the free end fed to an outlet from the chamber. This gives even treatment of the material over its full length and enables the time of treatment to be made as long as desired. C. O. C.

Applying Uniform Pressure along the Length of Squeeze Rollers. Lindauer Dornier. *BP* 737,337

Reducing Noise in Suction Apparatus of Fabric Drying Machines, etc. Bowaters Development & Research. *BP* 736,149

Coating Open-width Material with Vapour, Liquid or Paste. A. R. Trist. *BP* 736,747

The material is supported on a moving resilient bed. A stationary pressure resisting trough containing the coating material has its mouthpiece sealed by the material. There are means for discriminate leakage of the coating material from the mouthpiece. The coating material is forced under pressure from the trough onto the material, the amount applied being controlled by a springy lip forming part of the mouthpiece and trailing lightly on the material. C. O. C.

Printing Flexible Webs. Timsons. *BP* 737,315

A compact high-speed machine whose various units or components are completely accessible from outside the machine. C. O. C.

Continuous Printing and Flocking. United Merchants & Manufacturers. *USP* 2,695,244

A machine in which cloth or the like can be printed and/or flocked in one run through the machine. C. O. C.

Applying Strips or Bonds of Coating to Sheet Material. W. Hesselmann. *BP* 738,263

A reservoir has a lower dispersing slit. A bent piece of foil partly covers the slit and has one or more holes to enable the coating material in the reservoir to issue through the slit. The thickness of the foil determines the thickness of the coating and the shape of the holes the width of the coating. C. O. C.

Apparatus for Storing Printing Rolls, etc. in Upright Position. C. F. Moore & Sons. *BP* 737,003

Embossing Roll. Grote Manufacturing Co. *BP* 734,643

A polished metal roll has cavities produced in its surface by pressing against it clean fire-polished glass beads. The roll is then used for embossing plastic sheet so as to produce on it a multiplicity of lens formations suitable for reflex reflecting purposes. C. O. C.

Embossing Machine. Black–Clawson Co. *USP* 2,696,638

A machine in which the pattern embossed on the material can be changed without stopping the passage of the material through the machine. It is particularly applicable to the production of plastic films. C. O. C.

Injection Device for Laundry Washing Machine. Société Anonyme des Usines Jean Gallay. *BP* 735,850

An injection device for laundry washing machines provides a jet or jets of water sufficiently powerful to rotate the water and washing in the tub. The injection ducts are so arranged that there is minimum loss of pressure due to the water having to change direction

suddenly as it passes vertically up the outside and then vertically down into the tub, thus economising on power needed to drive the pumps. J. W. B.

Machine for Applying Circles of Ink or the like around Cylindrical Objects. R. P. Scherer Corpn. *BP* 737,686

Printing of Shaped Articles. C. H. Priestley and G. L. Murray. *BP* 737,461

Colour is screen printed onto a flat sheet and is then offset onto the articles to be printed by means of an intermediate member which takes up the colour from the sheet and deposits it onto the surface to be printed. C. O. C.

Printing or Decorating Ceramic Ware. G. L. Murray. *BP* 736,312

Machine embodying the principle described in *BP* 735,637 (*J.S.D.C.*, **71**, 689 (Nov. 1955)). C. O. C.

Carbon Black. United Carbon Co. Inc. (Maryland). *BP* 738,346

Apparatus enabling improved control of the quality and yield. C. O. C.

Jig. Celanese Corpn. of America. *USP* 2,696,421

Uniformity and levelness of dyeing across the entire width of the fabric is obtained by tilting the material as it leaves the dye liquor and/or the roller onto which it is being wound. This may be achieved by tilting the whole jig alternately in opposite directions across the width of the fabric, the change in tilt accompanying the change of direction of running of the fabric. C. O. C.

Milling Machine. Seedhill Finishing Co. *BP* 737,664

A mouthpiece to guide the fabric into the nip is placed at the inlet to the nip and has an entry which curves gently and smoothly outwardly and downwardly toward the direction the fabric takes in coming from the trough. This obviates need for an idler roller. C. O. C.

Automatic Control of Jigs and Similar Machines where Fabric is alternately Wound on and off Two Rollers. Celanese Corpn. of America. *BP* 738,548

A revolution counter is present to stop the drive to the first roller and start that of the second after a certain number of revolutions. A second counter similarly stops the drive of the second roller and starts that of the first. Both counters are so driven by the first roller that while one counter is counting away from its preset stopping position, the other is counting towards its preset stopping position. C. O. C.

Embossing. F. A. Sunderhauf and J. C. O'Hear. *BP* 737,440

The tendency for a non-uniform pattern to be produced when using mated engraved embossing rolls is avoided by allowing a clearance space between the bottom and sides of the recesses of the engraved surface of the female roll so that material is kept with only partial contact with the bottoms and sides of those recesses while it is being embossed. C. O. C.

Continuous Scouring of Cotton (VII p. 750).
Ultrasonic Tanning and Dyeing (VIII p. 752).
Use of Silicones in the Textile Industry (X p. 755).

II—WATER AND EFFLUENTS

Treatment and Disposal of Ammoniacal Liquors. W. H. Blackburn. *Chem. and Ind.*, 1228–1232 (1 Oct. 1955).

PATENT

Water Softening and Scale Reducing Devices. Main Water Heaters. *BP* 736,014

A cylindrical container is externally threaded at one end so that it can be fixed in one aperture of a T piece, the other two apertures being connected to delivery and feed water supply pipes respectively. The container is charged with a suitable water softening or de-scaling composition, e.g. sodium metaphosphate, held in by a gauze and with an access channel to the water supply. This is covered by a spring-loaded valve which is forced open when the container is screwed into the T piece by virtue of a spindle projecting from the valve head to the base of the container: thus, when the container is unscrewed the valve is forced shut, thus permitting interchange and renewal of the softener without cutting off the water supply. J. W. B.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Phosphates and their Uses in Textiles. F. Kroemer. *Melliand Textilber.*, **36**, 832–834 (Aug.); 947–951 (Sept. 1955).

The phosphates are divided into—I uncondensed, e.g. orthophosphate; II straight-chain condensed, e.g. hexametaphosphate; and III cyclic condensed, e.g. tri- and tetra-metaphosphate; and their properties are tabulated. In the first part of the paper the applications of orthophosphates are considered. Recommendations are made in the second part for the selection of specific phosphates for sequestration, detergent building, peptisation, dispersing, and resistance to boiling. S. R. C.

Fatty Acid Derivatives of Diethanolamine. J. R. Trowbridge, R. A. Falk, and I. J. Krems. *J. Org. Chem.*, **20**, 990–995 (Aug. 1955).

Soak Grease and Lanolin. J. Valléo. *Teintex*, **20**, 681–700 (Sept. 1955).

A review of the methods of purification, the derivatives obtained, and the applications of the latter. 135 references are given. S. R. C.

Mesomorphic Behaviour of Anhydrous Soaps. I—Light Transmission by Alkali-metal Stearates. D. P. Benton, P. G. Howe, and I. E. Puddington. *Canadian J. Chem.*, **33**, 1384–1391 (Sept. 1955).

Conductivity of Aqueous Potassium Dodecyl Sulphonate at Various Temperatures and with Solubilised Benzene. Wei-chuwan Lin. *Bull. Chem. Soc. Japan*, **28**, 227–230 (April 1955).

The critical micelle concentrations (C.M.C.) of potassium dodecyl sulphonate have been determined at temperatures between 25°c. and 60°c. over a range of concentrations of benzene by conductometric measurements. It has been found that the effect of increasing concentration of benzene is to lower the C.M.C. and that the C.M.C. also becomes smaller as the temperature rises, as has previously been noted by other workers for long-chain sulphonates. Benzene has no effect on the conductivity at concentrations of the dodecyl sulphonate up to the C.M.C., but in the critical region there is a marked effect, which decreases as the concentration of surfactant is further increased. W. J. M.

PATENTS

Detergent for Scouring under Acid Conditions. Monsanto. *BP* 738,278

The concentrated aqueous solutions of alkylaryl sulphonate obtained in presence of an alkylene oxide surface active agent are very effective detergents under acid conditions being especially effective when used on wool. C. O. C.

Detergent. General Aniline. *BP* 738,538

A residue of (1) a water soluble chloride, sulphate, nitrate, bromide or acetate of a polyvalent metal and (2) a compound of formula $R{\cdot}O(CH_2{\cdot}CXHO)_n{\cdot}SO_3M$ (R = branched chain Alk or alkylaryl of > 9 C; X = H or CH_3; M = a monovalent water solubilising cation; n = 1–8) e.g. *iso*octylphenol + 4 mol. ethylene oxide sodium sulphate, has much better foaming and detergent properties than the polyoxyalkylene compound alone. C. O. C.

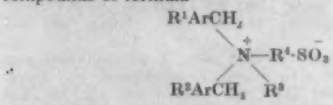
Detergent Composition. H. F. Johnston. *BP* 737,824

A detergent composition with the appearance of soap and resistant to hard water and sea water is made from a mixture of commercial stearic acid, a sulphonated fatty oil, Na or K silicate, NaOH or KOH, an alkyl benzene sulphonate in paste form, and water, with or without a sulphated fatty alcohol, the proportions to result in a 4–19% fatty acid content. In one example a solid general purpose cleanser comprises sulphonated fatty oil (10%), alkyl benzene sulphonate (15), NaOH (1), KOH (1), 140°Tw. sodium silicate (5), sodium metasilicate (10), commercial stearic acid (15), kaolin (20), and water (23).

The temp. should not exceed 195°F. and the liquid material can be poured into moulds and allowed to set. J. W. B.

Quaternary Taurine Type Surface-active Agents. California Research Corpn. *USP* 2,697,116

Treatment of a molar excess of an alkyl arylmethylene halide or an arylmethylene halide with an *N*-alkyl amino alkane sulphonate in presence of a neutralising agent yields compounds of formula—



(R^1 and R^2 = H or Alk of 1–24 C; R^3 = Alk of 1–7 C; R^4 = alkylene of 1–7 C), e.g. *N*,*N*-dibenzyl-*N*-methyltaurine, are amphoteric surface-active agents. C. O. C.

Benzine Soap. Californian Research Corpn. *USP* 2,697,075

Effective dry-cleaning detergent, water-emulsifying compositions are made by dissolving in Stoddard solvent a surface-active nonionic polyoxyalkylene ether of a monoalkyl phenol (Alk averages 14 C; polyoxyalkylene contains 5–7 ethylene oxide units). About 15–25% by wt. of the ether on the weight of the solvent is used. Such a solution added to the bulk of the dry cleaning liquor not only enhances its cleansing action but enables water to be finely emulsified in the liquor. C. O. C.

Reacting Fatty Acid Chlorides with Proteins—Auxiliary Products. Armour & Co. *BP* 736,584

Esterified proteins with a wide variety of uses, including those of waterproofing, adhesives and detergency, are prepared by a method in which proteins or their hydrolysis products are fully reacted with fatty acid halides. The protein is treated with an oxidising agent capable of hydroxylating the free amino groups, and the product is reacted with a fatty acid halide of 1–22 C. In one example an effective detergent is produced by hydrolysing hair with aqueous NaOH, concentrating the hydrolysate, oxidising it with peracetic acid, and esterifying with stearyl chloride. J. W. B.

Silica Aquasols for rendering Cellulose Fibres Resistant to Slipping. Monsanto. *USP* 2,696,444

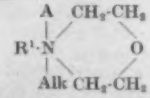
An alkaline silica aquasol containing a water-soluble condensate of an alkylene oxide (e.g. ethylene oxide) and an ester of a fatty acid of 10–20 C (e.g. oleic acid) with a polyhydric alcohol of 3–6 C and 3–6 OH (e.g. sorbitan) is applied to cellulose fibres after carding to improve their inter-fibre friction. C. O. C.

Size. ICI. *BP* 737,691

Polytriethylene glycol adipamide applied from aqueous solution is an excellent size for yarns, etc. C. O. C.

Oil-soluble Cationic Antistatic Agent. Atlas Powder Co. *USP* 2,695,270

A combined lubricant and antistatic agent consists of a compound of formula—



(R^1 = Alk of 11–20 C; A = anion), e.g. cetylethyl morphinolinium ethosulphate, dissolved in oil by the aid of a compound of formula $R^2(C_2H_4O)_xH$ (R^2 = undecyl, lauryl, myristyl, cetyl, oleyl or stearyl, or a mixed fatty and/or rosin acid radical; x = 4–20), e.g. 4 polyoxyethylene stearic acid. C. O. C.

Softening Agents. Monsanto. *USP* 2,695,243

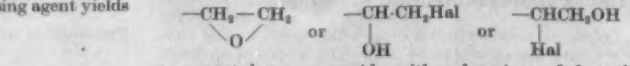
Condensing alkylenepolyamines with an incompletely chlorinated paraffin wax yields liquid to waxy solids which are readily emulsified in water to yield softening agents for textiles. C. O. C.

Wetting Agents for use in Mercerising Lye. FBy. *BP* 734,749

Those sulphonamides of low mol. wt. paraffins which are soluble in mercerising lye impart to the lye excellent wetting properties. Thus if to 100 parts mercerising lye are added 1–2 parts of an alkyl sulphonamide (Alk of 5–7 C) and 2 parts of glycerol-diethyl ether, the lye wets cotton immediately. C. O. C.

Dyebath Assistants and Stripping Agents. S. *BP* 738,306

The products obtained by treating an ether of formula $R^1O{\cdot}CH_2X$ (R^1 = an aliphatic or hydroaromatic radical of > 7 C or alkylated aromatic hydrocarbon radicals containing at least one Alk of > 4 C, the aliphatic hydrocarbon chain can be interrupted by hetero groups; X =



e.g. *n*-octyloxyproperoxide with polyamines of formula $R^2NH{\cdot}[A{\cdot}NR^3]_n{\cdot}A{\cdot}NR^4R^5$ (R^3,R^3,R^4 and R^5 = H, Alk, hydroxyalkyl or ether residues; A = alkylene of 2–4 C; n = 0 or an integer, if n = 0 then at least one of R^2, R^3, R^4 or R^5 must be other than H), e.g. diethylenetriamine, followed if desired by alkylating or aralkylating, are soaplike products stable to acid and alkali. They are excellent levelling, penetrating, and stripping agents for direct, acid, basic, chrome and vat dyes. C. O. C.

Melamine–Formaldehyde Syrups. British Oxygen Co. *BP* 738,033

A syrup which remains clear and mobile for at least several months consists of a solution in water or a water/alcohol mixture of > 80% by weight of a melamine-formaldehyde condensate in presence of borax. The amount of borax should be equivalent to 0·01–2·0% of $Na_2B_4O_7$ on the weight of melamine and formaldehyde used. The molar range of melamine : formaldehyde should be from 1 : 1 to 1 : 6. C. O. C.

Stabilising Agents for Resinous Finishing Compositions. BASF. *BP* 735,861

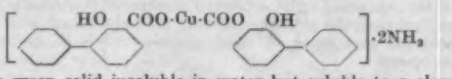
Basic reacting acyl derivatives of a hydroxyalkylamine or polyamine (aliphatic chain of < 7 C; acyl of 12–20 C) containing at least 1 reactive H atom, e.g. condensate of 1 mol. of stearic acid with 1 mol. of dihydroxyethyl diethylene triamine, added to aminoplast-forming methylol compositions stabilise them against long storage. C. O. C.

Soluble Dicyandiamide–Formaldehyde Condensate. Jacques Wolf & Co. *BP* 736,197

An aqueous solution of dicyandiamide, formaldehyde and a water-soluble, surface active anionic sulphonate is heated, the final heating being continued at pH > 7 until the condensate is not precipitated when diluted with water but precipitates readily on addition of an acid substance, particularly $Al_2(SO_4)_3$. The product is particularly suitable for impregnating fibrous products. C. O. C.

Copper 3-Phenylsalicylate–Ammonia Addition Product for Rotproofing Cellulosic Material. Dow Chemical Co. *USP* 2,695,858

The copper 3-phenylsalicylate-ammonia addition product represented by the formula—



is a green solid insoluble in water but soluble to a clear dark blue solution in aqueous ammonia. It is prepared by treating 1 mol. copper 3-phenylsalicylate with 2 mol. of ammonia in aqueous solution and evaporating to dryness at room temperature. Application of < 0·5% by wt. of it to cellulosic materials renders the material rotproof. C. O. C.

Organomercury Fungicides. Ward Blenkinsop & Co. *BP* 736,399

Phenyl mercury 8-hydroxyquinolate or its halogenated derivatives containing one or two halogen atoms in the carbocyclic nucleus are effective rotproofing agents suitable for application to textiles or incorporation in paints. C. O. C.

Organosilicon Water-repellent Compositions for Leather. Midland Silicones. *BP* 736,378

Any type of leather may be rendered resistant to penetration by water by treating it with a mixture of (1) 15–20% by wt. of a hydrolysable compound of formula $Ti(OR^1)_4$ (R^1 = Alk of < 13 C or hydroxylated Alk of < 13 C and < 4 OH groups), (2) 5–20% by wt. of a methylsiloxane copolymer made up of trimethylsiloxane

and SiO_2 units so that CH_3:Si::1·0–2·5:1, and (3) 15–80% by wt. of a polysiloxane of formula—

$$R^2_nSiO_{\frac{4-n}{2}}$$

(R^2 = Alk or alkaryl of < 4 C or monocyclic Ar; n = on average 2·0–2·9). C. O. C.

Solution for Rendering Cellulosic Materials Fire-resistant. Titan Co. *BP* 735,041

A carboxylic acid is treated with $TiCl_4$ and Sb_2O_3 in presence of water so as to produce a solution containing 120–160 g. Ti per litre. For each mol. of Ti there are 1–3 mol. of acylate, 0·6–1·0 mol. of Sb and 1·0–3·0 mol. chloride and for each mol. of Sb an additional 3 mol. of chloride. The solution is stable and effective even after being stored for 2 months. C. O. C.

Rotproofing Agents. Riedel-de Haën. *BP* 737,247

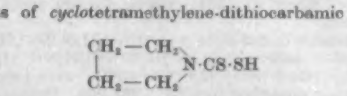
Organic mercuric salts of a hydroxyquinoline, the organo mercury radical being linked by an ionic bond to the O atom of the hydroxyquinoline, e.g. the phenyl mercuric derivative of 5-chloro-8-hydroxyquinoline are potent rotproofing agents which are applicable from many organic solvents or from aqueous dispersion. They are brightly coloured but otherwise suitable for use on textiles. C. O. C.

Organomercury Dicarboxylate Rotproofing Agents. Nuodex Products Co. *BP* 737,826

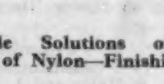
Compounds of formula $R^1HgOOC{\cdot}CH_2{\cdot}CHR^3{\cdot}COOHgR^1$ (R^1 and R^3 = organic residues linked directly to the Hg atom through a C atom; R^3 = hydrocarbon of > 7 C), e.g. di(phenylmercury)dodecenyl succinate, are rotproofing agents which are particularly suitable for use in paints, etc. C. O. C.

Fungicides and Insecticides. BASF. *BP* 737,277

Such thiocarbamic acids and their derivatives as contain *cyclo*tetramethylene groups, especially *cyclo*tetramethylenethiuram disulphide—



and salts of *cyclo*tetramethylene-dithiocarbamic acid—



are especially effective water-soluble fungicides and insecticides. C. O. C.

Water-dispersible Solutions of *N*-Alkoxyalkyl Derivatives of Nylon—Finishing Agents. Hans C. Bick. *BP* 734,791

A mixture of an alcohol-soluble *N*-alkoxyalkyl derivative of nylon, a non-ionic emulsifying agent and sucrose octa-acetate dissolved in an aqueous solution of a water-miscible alcohol yields a solution which is readily dispersible in water. Nylon material treated with such a solution, if desired with addition of other finishing agents, and then dried is enabled to absorb and disperse moisture much faster than untreated material and so does away with the feeling of stickiness or clamminess usually associated with nylon garments. When such a solution is applied to cotton, improved resistance to abrasion results. The finish resists washing. C. O. C.

Solutions of Acrylonitrile Polymers. Chemstrand Corpn. *USP* 2,695,278

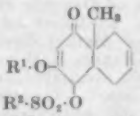
Low viscosity solutions of fibre forming acrylonitrile polymers are obtained by mixing the polymer with an organic solvent in presence of 0·1–5·0% on the wt. of the solvent of nitric, hydrochloric, or sulphamic acid. C. O. C.

1-Methyl-2-pyridone as Solvent for Acrylonitrile Polymers. Chemstrand Corpn. *USP* 2,696,478

The polymer is dispersed in 1-methyl-2-pyridone and then heated with agitation until a clear homogeneous solution is obtained. C. O. C.

Plasticisers for Cellulose Nitrate. Monsanto. *BP* 738,136

Compounds of formula—



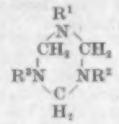
(R^1 = Alk of 1–5 C; R^2 = aromatic hydrocarbon, camphoryl or halogeno camphoryl), e.g. DL-*trans*-1:4:4a:5:8:8a-hexahydro-2-methoxy-4a-methyl-4-keto-naphthalene-1-(*p*-tosylate), are high melting point solids useful as plasticisers for cellulose nitrate. C. O. C.

Plasticisers for Vinyl Resins and Cellulose Derivatives. General Aniline. *BP* 737,929

Liquid polyesters of dicarboxylic acids with 1:4-butanediol or 1:6-hexanediol, the polyesters have at the end of their chain a monocarboxylic radical of 2–18 C, are excellent plasticisers for vinyl resin and cellulose esters and ethers. Suitable acids are succinic, maleic and tetrahydrophthalic. C. O. C.

Gas Fume Fading Inhibitors. Celanese Corpn. of America. *BP* 737,947

Compounds of formula—



(R^1, R^2 and R^3 = hydrocarbon radicals in which a β-C atom is joined by a single bond to an aliphatic α-C atom and by a double bond to a v-C atom), e.g. tribenzyltriethylene triamine, are excellent gas fume fading inhibitors which can be used in the dyebath. They have good fastness to washing and dry cleaning and do not discolour on exposure to light or gas fumes. C. O. C.

Acrolein–Formaldehyde Condensate for Imparting Crease-shedding Properties. Dan River Mills. *USP* 2,696,477

Acrolein (1 mol.) is treated with formaldehyde (1–6, preferably 4, mol.) in presence of a basic catalyst, e.g. Na_2CO_3, while keeping the mixture at 50–65°c. The product is used in aqueous solution for imparting crease shedding properties to cloth. C. O. C.

Chromium Complexes of Fluorocarbon Acids—Hydro- and Oleo-phobic Finishing Agents, Coatings and Films. Minnesota Mining & Manufacturing Co. *BP* 738,065

A reactive soluble colloidal chromiferous compound is treated in presence of a hydroxylated compound and in absence of Cl or compounds containing Cl with a perfluoroalkyl monocarboxylic acid of 4–12 C. Thus, 1 mol. of CrO_3 is treated with 2 mol. of perfluorocaprylic acid, $CF_3(CF_2)_6COOH$ in aqueous medium containing a reducing agent, e.g. methanol or *iso*propanol. The whole is heated until the product is free from dissolved acid and is no longer soluble in methanol but is soluble in *iso*propanol. The product is soluble in highly fluorinated solvents, e.g. Freon 12 (dichlorodifluoromethane). They are used as finishing and coating agents for textiles, and for making self-sustaining films. Fabric and paper treated with them in such small amounts as to impart no colour or alteration of handle are very impervious to staining with aqueous or oily liquids. They may be used on all types of fibres without fear of causing tendering. C. O. C.

Tetrabenzylmethylenediamine as Gas Fume Fading Inhibitor (VIII p. 752).
Alkylated Polyamines for imparting Improved Fastness to Wet Processing to Direct Dyes (VIII p. 752).
Condensates of Complex Copper Compounds with Nitrogenous Compounds and Aldehydes (VIII p. 752).
Use of Silicones in the Textile Industry (X p. 755).
Acidic Organic Mercurial Composition for Rotproofing Papermaking Stock (XI p. 756).
Factors influencing Emulsion Stability and Viscosity (XV p. 760).

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Electronic Spectra of Organic Molecules and their Interpretation. I—Effect of Terminal Methyl and Substituted Methyl Groups of Conjugated Systems on *K*-Bands. A. Burawoy and E. Spinner. *J.C.S.*, 2557–2563 (Aug. 1955).

Structural modifications of a terminal group which increase its polarisability or the polarity of the absorbing system are found to displace the *K*-band to longer wavelengths, and the dependence of the energy of transition on the facility of the electron migration in one direction of the absorbing conjugated system is demonstrated. Single bonds of the substituted methyl groups (A·CH_3) participate in the electron migration of the transition and, in favourable cases, cause red-shifts comparable to those brought about by an additional conjugated double bond (A:CH). These results are accounted for by inductomeric displacements of "localised" electrons. H. H. H.

Mills–Nixon Effect and Bond Multiplicity via Ultraviolet Spectra. R. H. Horning and E. D. Amstutz. *J. Org. Chem.*, **20**, 1069–1085 (Aug. 1955).

Oxidation of Phenols with Iodosoacetates. A. Siegel and F. Antony. *Mh. Chem.*, **86**, 292–300 (April 1955).

Synthesis of Methyl Homologues of Naphthols and Dihydroxynaphthalenes. Ng. Ph. Buu-Hoï and and D. Lavit. *J.C.S.*, 2776–2779 (Aug. 1955).

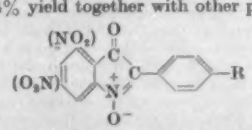
Such methods as are known for the introduction of a methyl group into a β-naphthol cannot be extended to α-naphthols or dihydroxynaphthalenes, and they also involve tedious separations. It has now been found that methyl groups can readily be introduced into the above compounds by a three-stage synthesis; viz. by formylation of the corresponding methyl ethers, Wolff–Kishner reduction (Huang-Minlon's technique, *J. Amer. Chem. Soc.*, **68**, 2487 (1946)) of the naphthaldehyde and demethylation with pyridine hydrochloride. This gives excellent overall yields of 1-methyl-2- and 4-methyl-1-naphthol and 1-methyl-2:6- and 1-methyl-2:7-dihydroxynaphthalene. The reaction sequence can be repeated, and from the last three substances 2:4-dimethyl-1-naphthol and 2:6-dihydroxy-1:5- and -2:7-dihydroxy-1:8-dimethylnaphthalene respectively are easily obtained. H. H. H.

Benzylations of Phenols and Naphthols catalysed by Zinc Chloride. Ng. Ph. Buu-Hoi and P. Demerseman. *J. Org. Chem.*, **20**, 1129–1134 (Aug. 1955).

Nitration of *o*-Acetamidoethylbenzene. C. Hansch. *J. Org. Chem.*, **20**, 1026–1029 (Aug. 1955).

Photochemical Behaviour of some *o*-Nitrostilbenes. J. S. Splitter and M. Calvin. *J. Org. Chem.*, **20**, 1086–1115 (Aug. 1955).

2-Nitrostilbenes, which may carry further nitro groups in the 4 and 6 positions and which are substituted in the 4′ position by electron-releasing groups, when irradiated by sunlight are converted into the corresponding isatogens (I) up to a 44% yield together with other products—



I: R = H, Cl, O·CO·CH_3, O·CH_3, OH, or $N(CH_3)_2$

The reaction consists of two phases—the disappearance of the stilbene by absorption of light and a subsequent thermal dark reaction. The structure of the intermediates and the mechanism of the process are discussed. H. E. N.

Nitro-, Nitroso-, and Azo-pyrazoles. R. Hüttel, F. Büchele, and P. Jochum. *Chem. Ber.*, **88**, 1577–1585 (Oct. 1955).

Aromatic Azo Compounds. VII—Synthesis and Absorption Spectra of some Azoquinolines. G. M. Badger and R. G. Buttery. *J.C.S.*, 2816–2818 (Aug. 1955).

The 2:2′-, 4:4′-, 5:5′-, 6:6′-, and 7:7′-azoquinolines have been synthesised for comparison with the carcinogenic 2:2′-azonaphthalene. The last three were obtained by sulphite reduction of the diazotised 5-, 6-, and 7-aminoquinolines; 2:2′-azoquinoline was prepared by an improved Marckwald and Meyer's method (*Ber.*, **33**, 1885 (1900)); viz. oxidation of the hydrazo compound from 2-chloroquinoline and hydrazine hydrate, and adaptation to 4-chloroquinoline afforded the 4:4′-azoquinoline. The absorption spectra are compared with those of the azonaphthalenes and the phenylazonaphthalenes. H. H. H.

The Irgalan Dyes—Neutral-dyeing Metal-complex Dyes. G. Schetty. J.S.D.C., **71**, 705–724 (Dec. 1955).

The chemistry of chromium-complex dyes is discussed in relation to dyeing properties on wool, with particular reference to the problem of avoiding skittery dyeing arising from differences between individual wool fibres. The structural features required for dyes to give non-skittery dyeings under neutral conditions are deduced, and it is shown how these researches resulted in the production of the Irgalan dyes. AUTHOR

Polyvinylaminobenzaldehyde Azo Dyes. E. Minami and S. Kojima. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 826–7 (1954): *Chem. Abs.*, **49**, 10628 (10 Aug. 1955).

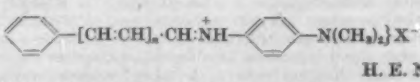
m-Nitrobenzaldehyde was treated with excess ethylene glycol in presence of 63% H_2SO_4 in a water bath for 6–8 hr. and the resulting *m*-nitrobenzaldehyde ethylene acetal (I) recrystallised from methyl alcohol to give a 97% yield. Boiling I with Na_2S in methyl alcohol in presence of HCl for 6 hr. gave a 33% yield of *m*-aminobenzaldehyde ethylene acetal (II), a yellow-orange liquid. Polyvinyl alcohol (1 g.) was treated with II (1 g.) in water (40 c.c.), acidified with HCl at room temperature gradually raised to 50°c. in 1 hr., heated at 45–50°c. for 4 hr., poured into methyl alcohol, the HCl neutralised with NaOH, and the white precipitate extracted with methyl alcohol for 6 hr. and finally dried. The resulting compound was 30% acetalised. When coupled with phenol, *o*-cresol, resorcinol, 1- or 2-naphthol, aniline, *N*-methylaniline, *o*-toluidine, *m*-phenylenediamine and 1- or 2-naphthylamine, it yielded yellow to red azo dyes of good fastness to washing and rubbing on Vinylon. C. O. C.

Synthesis of Dyes containing Acetal Groups and their Affinity for Vinylon. N. Kuroki, K. Wakamatsu, and K. Konishi. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57** 867–9 (1954): *Chem. Abs.*, **49**, 10628 (10 Aug. 1955).

The orange to red dyes *p*-(*p*-$O_2NC_6H_4N{:}N)C_6H_4NHCH_2(OC_2H_5)_2$ and *p*-(*p*-$RC_6H_4N{:}N)C_6H_4N(C_2H_5)CH_2CH(OC_2H_5)_2$ (R = NO_2CH_2CO or CHO) were prepared by the method described in *USP* 2,234,703. They yield deep fast dyeings on Vinylon from a HCl bath. Probably there is some covalent bonding between the dye and the polyvinyl alcohol fibres. C. O. C.

Colour Reactions of Unsaturated Carbonyl Compounds. IV—Constitution of Coloured Salts of Anils. S. Hünig and J. Utermann. *Chem. Ber.*, **88**, 1485–1491 (Oct. 1955).

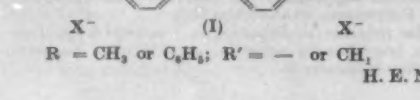
Study of alkyl derivatives indicates that the salts have the structure—



H. E. N.

Bis(2:3-*o*-diphenylenetetrazolium Salts). D. Jerchel and H. Fischer. *Chem. Ber.*, **88**, 1595–1599 (Oct. 1955).

Ultraviolet radiation smoothly converts bis(2:3-diphenyltetrazolium salts) into bis(2:3-*o*-diphenylenetetrazolium salts) (I). Reduction with dithionite or hydrazine leads to radicals, but catalytic hydrogenation yields bis(3:4-benzocinnoline)s.

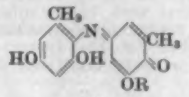


R = CH_3 or C_6H_5; R′ = — or CH_2

H. E. N.

Structure of a Constituent of Orcein. J. F. W. McOmie and J. M. White. *J.C.S.*, 2619–2623 (Aug. 1955).

Condensation of 6-methoxy-*p*-toluquinone 4-chloroimide with orcinol in alkaline solution indicates formation of the sterically hindered indophenol (I: R = CH_3), whose instability, together with the failure of the appropriate reaction to give the trihydric phenol (I: R = H), makes unlikely Liebermann's structure (I: R = H) for one of the purple compounds isolated from the mixture (orcein) given by the action of air and ammonia on orcinol (cf. *Ber.*, **8**, 1649 (1875)).



(I)

H. H. H.

Carboxylic Blue and Black Sulphur Dyes for Vinylon. N. Kuroki, A. Takaoka, E. Ota, and K. Konishi. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 864–6 (1954): *Chem. Abs.*, **49**, 10628 (10 Aug. 1955).

Aniline, *o*-toluidine, *N*-ethylaniline or *N*-2-hydroxyethylaniline (0·5 mole) were each refluxed on a sandbath in presence of glacial acetic acid (5 g.) and hydroquinone (0·1 g.). Vacuum distillation yielded $C_6H_5NHCH_2CH_2COOCH_3$, *o*-$CH_3C_6H_4NHCH_2CH_2COOCH_3$, $C_6H_5N(C_2H_5)CH_2CH_2COOCH_3$ and $C_6H_5N(CH_2CH_2OH)CH_2CH_2COOCH_3$ which were converted into indophenols by the method described in *Chem. Abs.*, **49**, 4298 (1955). Treatment of these indophenols with Na_2S and S yielded blue dyes having good affinity for Vinylon. C. O. C.

Syntheses of Organic Fluorescent Compounds. XXX—Rearrangement of the Sulphonic Acid Group when Sulphonating 3:6-Dinitrocarbazole. Z. Yoshida. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 238–241 (1954); **XXXI—Influence of Steric Hindrance on the Emissivity of Fluorescence in 3:6-Diaminocarbazole Derivatives.** *Ibid.*, 241–3: *Chem. Abs.*, **49**, 11620 (10 Sept. 1955).

XXX—3:6-Dinitrocarbazole was treated with conc. H_2SO_4 at 95–98°c. for 10–15 min. and for 7 hr. Na salts of the monosulphonates obtained by both methods were treated with the Borodkin benzidine reagent (*Chem. Abs.*, **43**, 973 (1949); **46**, 7092 (1952)) and formation of benzidine salt used to indicate the structure of the sulphonates. It seems that sulphonation occurs first in the 1-position and then, with longer treatment, in the 2-position.

XXXI—Examination of the fluorescence of various derivatives of 3:6-diaminocarbazole and 3:6-di(methylamino)carbazole showed that sulphonation *o-* to the amino groups, i.e. at 2- and 7-positions results in a steric hindrance effect on the intensity of the fluorescence. C. O. C.

Sulphur Dyes for Vinylon from *N*-Arylmorpholine. N. Kuroki, A. Katayama, J. Nishino, and K. Konishi. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 863–4 (1954): *Chem. Abs.*, **49**, 10627 (10 Aug. 1955).

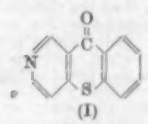
Three *N*-arylmorpholine indophenols, N-(4-morpholinophenyl)-*p*-benzoquinone imine (I), *N*-(3-methyl-4-morpholinophenyl)-*p*-benzoquinone imine (II), and *N*-(4-morpholinophenyl)-1:4-naphthoquinone imine (III) were prepared by condensing *N*-phenylmorpholine, *N*-*o*-tolylmorpholine, and *N*-(*p*-aminophenyl)-morpholine, respectively, with *p*-nitrosophenol (for I and II) or 1-naphthol (for III). Treating I and II with Na polysulphide yielded blue dyes, while III gave a violet dye. The blue dyes had good affinity for cotton and Vinylon but yielded dull dyeings. The violet dye gave clear dyeings on Vinylon but had no affinity for cotton. C. O. C.

Condensation of 8-Amino-1-aza-anthraquinone and 1-Halogenoanthraquinone. M. Yokote, I. Fukashima, J. Matsumara, and R. Ito. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 195–6 (1954): *Chem. Abs.*, **49**, 10627 (10 Aug. 1955).

Imide condensation between 0·1 g. 8-amino-1-aza-anthraquinone (I) and 0·23 g. 1-bromoanthraquinone was carried out in presence of 0·19 g. K_2CO_3, 0·02 g. $CuCl_2$ and 2·57 g. naphthalene, in a CO_2 atmosphere at 210°c. for 12 hr. After cooling, the precipitate in hot C_2H_5OH was dissolved in *o*-dichlorobenzene (II). The red-violet substance (0·033 g.) soluble in II became brownish green in conc. H_2SO_4 and dyed cotton greyish red-violet. The absorption spectra of this compound showed absorption maxima at 3500 and 5200 A. quite similar to that of 1:1′-dianthrimide. A dark grey compound was also obtained as a by-product. I (0·12–0·56 g.) was similarly condensed with 0·13–0·61 g. of 1-chloroanthraquinone in II, nitrobenzene or naphthalene in presence of 0·13–0·63 g. anhydrous sodium acetate and 0·03–0·14 g. $CuCl_2$ by boiling for 12–18 hr.; 0·1–0·14 g. of a grey cotton dye, dark brown in conc. H_2SO_4, was obtained. Similar treatment of I in naphthalene or nitrobenzene yielded a similar dark grey dye which is presumably a condensed compound of I and similar to the by-product described in the first reaction above. C. O. C.

Xanthones and Thioxanthones. VI—Preparation and Properties of 9-Thia-3-aza-anthrone. S. Kruger and F. G. Mann. *J.C.S.*, 2755–2763 (Aug. 1955).

4-Chloro-3-nitropyridine reacts violently with thiophenol to give 3-nitro-4-pyridyl phenyl sulphide, and this on reduction and treatment of the diazotised amino compound with KI gives 3-iodo-4-pyridyl phenyl sulphide. The latter reacts with *n*-butyllithium in toluene to give 3-carboxy-4-pyridyl phenyl sulphide, which, on treatment with $SOCl_2$ and cyclisation of the acid chloride with $AlCl_3$ in nitrobenzene, affords 9-thia-3-aza-anthrone (I), the remaining isomer in this thia series. 9-Oxa-3-aza-anthrone also has been synthesised, but only in low yield. Unlike its three isomers, I does not oxidise to the sulphone.



(I)

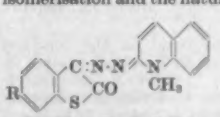
H. H. H.

Substituted Thionaphthens. C. Hansch and B. Schmidhalter. *J. Org. Chem.*, **20**, 1056–1061 (Aug. 1955).

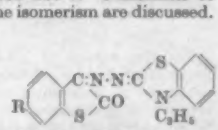
Dehydrogenation of 4-amino-2-mercaptoethylbenzene over a Cr–Cu catalyst at 445°c. gave 6-aminothionaphthen, converted by the Sandmeyer reaction into the 6-chloro cpd., which was also obtained from 6-chloro-3-hydroxythionaphthen by reduction with acetic acid and zinc dust. The 6-chloro cpd. differed from that designated as such by Sunthankar and Tilak (*Proc. Indian Acad. Sci.*, **32 A**, 396 (1950)), the latter now being identified as the 4-cpd., synthesised via 4-aminothionaphthen starting from thiophen and succinic anhydride. 6-Cyano-, 6-hydroxy-, and 6-carboxy-thionaphthen were also prepared from the 6-amino deriv. H. E. N.

***mero*Cyanines derived from Thio-oxindole. IV—The Isomerism of the Diazadimethin*mero*-cyanines.** R. H. Glauert and F. G. Mann. *J.C.S.*, 2537–2542 (Aug. 1955).

The probable *cis–trans* isomerism of four diazadimethin*mero*cyanines (types I and II) is found to be a common property which has not yet been detected in the analogous dimethin*mero*cyanines, although these exhibit a similar salt formation; e.g. the orange [3-(2:3-dihydro-2-oxothionaphthen)] [2-(3-ethylbenzothiazoline)] diazamethin*mero*cyanine (II: R = H), m.p. 175–176°c., is converted by boiling acetic acid or by HBr in cold acetone to a bright orange isomer of m.p. 259–260°c. Conditions of isomerisation and the nature of the isomerism are discussed.



(I: R = H, O-C_2H_5)

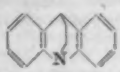


(II: R = H, O-C_2H_5)

H. H. H.

Steric Effects on Mesomerism. XIV— Basic Strength of Dibenzoquinuclidine and its Bearing on the Basic Strength and the Mesomeric Energy of Aromatic Amines. S. M. F. van der Krogt and B. M. Wepster. *Rec. Trav. chim.*, **74**, 161–167 (March 1955).

The mesomeric interaction between the amino group and the aromatic nuclei in dibenzoquinuclidine (I) is negligible as shown by its inability to couple with diazotised *p*-nitroaniline and its ultraviolet spectra, from which the characteristic absorption bands of aromatic amines are absent. The basic strength of I is approx. 3 pK_a units less than that of benzoquinuclidine because of the inductive effect of the extra phenyl nucleus, which is in agreement with earlier results.



(I)

C. H. R.

Melting and Crystallisation of Phenanthrene–Anthracene Mixed Crystals. A. Kofler. *Mh. Chem.*, **86**, 301–311 (April 1955).

Interaction between the Aromatic Chromophores in Polyphenyl Hydrocarbons. J. N. Murrell and H. C. Longuet-Higgins. *J.C.S.*, 2552–2556 (Aug. 1955).

It is shown that electron interaction between the chromophores in the linear *m*- and *p*-polyphenyls can account for the main features of their electronic spectra. A previous suggestion that the different characteristics of the spectra of the two series are due to conjugation in the *para*, but not in the *meta*, series is now shown to be probably a secondary effect, and the difference is interpreted without reference to conjugation between the aromatic rings. H. H. H.

Azabenzazulenes. I— 1-Azadibenz[*b,f*]azulene. C. W. Muth, D. O. Steiniger, and Z. B. Papaanastassiou. *J. Amer. Chem. Soc.*, **77**, 1006–1009 (20 Feb. 1955).

1-Azadibenz[*b,f*]azulene and the corresponding [*b*] and [*bh*] compounds have been synthesised by preparing the appropriate ketones, converting them to hydroazazulenes (indoles), and finally dehydrogenating. Azadibenzazulene—

is a red solid which was unaffected by daylight and the atmosphere when exposed on filter paper for 9 months. It is also stable when heated at 170–180°C. for 30 min.

C. O. C.

Derivatives of Fluorene. I— *N*-Substituted 2-Aminofluorene and 2-Aminofluorenone. T. L. Fletcher, M. E. Taylor, and A. W. Dahl. *J. Org. Chem.*, **20**, 1021–1025 (Aug. 1955).

Synthesis of Indenofluorenes. IV— The 2′:1′-2:3- and the 1′:2′-1:2-Compounds. L. Chardonnens and R. Ritter. *Helv. Chim. Acta*, **38**, 393–396 (March 1955).

[Synthesis of 4-Chloroisatin.] A. Romeo, H. Corrodi, and E. Hardegger. *Helv. Chim. Acta*, **38**, 463-467 (March 1955).

By the action of alkaline peroxide on the reaction product of 2-chloro-6-nitrotoluene and diethyl oxalate in presence of potassium ethoxide, 2-chloro-6-nitrophenylacetic acid is obtained. Reduction with ferrous hydroxide in ammonia affords 4-chloro-oxindole, which is oxidised to 4-chloroisatin with SeO_2. H. E. N.

Aromatic Hydrocarbons. LXX— Zethrene (1:12-6:7-Dibenzotetracene). E. Clar, K. F. Lang, and H. Schulz-Kiesow. *Chem. Ber.*, **88**, 1520–1527 (Oct. 1955).

This deep red, very reactive cpd. (I) is formed in the pyrolysis of acenaphthene (II) or acenaphthylene (III) and is present in III prepared by catalytic dehydrogenation of II. It is also obtained from III or diacenaphthylidene by reaction with NaCl–$AlCl_3$ above 130°C. Its structure was confirmed by synthesis from 2:8-dibromochrysene. The two central double bonds of I are fixed, but apparently this fixation has no effect on the absorption spectrum (compared with 1:2-7:8-dibenzoperylene) nor on its reactivity. Its first absorption band lies at 550 mμ. Coulson and Moser (*J.C.S.*, 1341 (1953)) having predicted 943 mμ. and Dewar (*ibid.*, 3539 (1952)) 660 mμ.

(I)

H. E. N.

Ferroverdin, a Green Pigment containing Iron produced by a Streptomycete. E. B. Chain, A. Tonolo, and A. Carilli, *Nature*, **176**, 645 (1 Oct. 1955).

Organic Pigments. II— Syntheses of 1-Phenyl-3-methyl-5-pyrazolone and its Derivatives. E. Koike, H. Iida, M. Okawa, and A. Kashioka. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 56–8 (1954); **III— Syntheses of 1-Phenyl-3-carboxyl-5-pyrazolone and its Derivatives.** E. Koike, H. Iida, and A. Kashioka. *Ibid.*, 123–5: *Chem. Abs.*, **49**, 11629 (10 Sept. 1955).

II— Phenylhydrazine (I) (24 g.) was added in 30 min. to a mixture of 60% ethyl alcohol (12 g.) and $CH_3COCH_2COOC_2H_5$ (II) (29·2 g.) at < 50°C., stirred for 2 hr., refluxed 4 hr. and filtered to yield 1-phenyl-3-methyl-5-pyrazolone (35·5 g.). Treating *p*-$ClC_6H_4NHNH_2$·HCl (6·5 g.) in water acidified with acetic acid with II (4·8 g.) gave an 84% yield of 1-(*p*-chlorophenyl)-3-methyl-5-pyrazolone. Other derivatives were similarly prepared.

III— Preparation of $(COCH_2COOC_2H_5)_2$, 1-phenyl-3-carboxy-5-pyrazolone, 1-phenyl-3-carboxyethyl-5-pyrazolone and some derivatives, and 1-phenyl-3-carbamide-5-pyrazolone, is described. They are intermediates for pyrazolone dyes. C. O. C.

Synthesis of Heterocyclic Pigments. I— Hydroxyquinoxaline and Dihydroxyphenazine Derivatives. S. Kawai, J. Kosaka, and M. Hatono. *Proc. Japan. Acad.*, **30**, 774–780 (1954): *Chem. Abs.*, **49**, 10973 (25 Aug. 1955).

2:3-Dinitroquinone dimethyl ether was reduced to the diamino compound (I) and then condensed with benzil. 5:8-Dimethoxy-2:3-diphenylquinoxaline (II) was obtained as yellow plates with greenish fluorescence. Condensing I with phenanthronequinone gave the orange-yellow 10:13-dimethoxy dibenzo [*a,c*] phenazine (III). This was dimethylated to the orange-red dihydroxy compound which could not be oxidised to the corresponding quinone but gave a blue ppt. with Pb (II) and a red-violet ppt. with Cu (II) but no ppt. with other metallic ions. II was dimethylated to the yellow dihydroxy compound which gave green-violet ppt. with Zn, violet with Pb (II) and dull green with Cu (II). C. O. C.

Syntheses of Heterocyclic Pigments. III— Synthesis of 2:3-Dimethyl-5:8-dihydroxyquinoxaline and the Influence of Light upon Catalytic Hydrogenation. S. Kawai, S. Tanaka, and K. Ichikawa. *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 40–3 (1954): *Chem. Abs.*, **49**, 10314 (10 Aug. 1955).

Recent Progress in Sensitising Dyes— II. S. Kimura. *Sci. Publs. Fuji Photo Film Co.*, (2) 115–154 (1954): *Chem. Abs.*, **49**, 10106 (10 Aug. 1955).

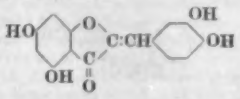
Review of the constitution, preparation and application of sensitising dyes recorded in *Chem. Abs.* from 1949–53. 210 references. C. O. C.

The Spectra of Malachite Green. P. Rumpf and M. Gillois. *Bull. Soc. chim. France*, 101–3 (1955): *Chem. Abs.*, **49**, 10059 (10 Aug. 1955).

Spectral study shows that the colour changes of Malachite Green with variation in the pH of the solution are caused by there being a mixture of several forms in equilibrium. In acid solutions a blue univalent cation and multivalent yellow cations contribute to the observed colour. At pH < 5 most of the derivatives substituted in the benzene nucleus are distinctly bluer with slight displacements of λ_{max} toward longer wavelengths.
C. O. C.

Anthochlor Pigments. X—Aureusin and Cernuoside. T. A. Geissman and J. B. Harborne. *J. Amer. Chem. Soc.* **77**, 4622–4 (5 Sept. 1955).

Aureusin and cernuoside are the 6- and 4-glucosides, respectively, of the orange-yellow pigment aureusidin, 3′:4′:4:6-tetrahydroxyaurone—



C. O. C.

Anthocyanins. Caracyanin, the Colouring Matter in the Bright Red Blossoms of *Canna generatis*. K. Hayashi, T. Noguchi, and Y. Abe. *Pharm. Bull.* (Japan), **2**, 41–5 (1954): *Chem. Abs.*, **49**, 10983 (25 Aug. 1955).

Caracyanin is shown to be 3-*O*-rhamnoglucosidylcyanin.
C. O. C.

Biochemical Study of Murex (Tyrian) Purple. S. Bouchilloux and J. Roche. *Bull. Inst. océanog.*, **52**, (1054), 1–23 (1955).

A Qualitative Theory of Metachromasy in Solution. M. Schubert and A. Levine. *J. Amer. Chem. Soc.*, **77**, 4197–4201 (20 Aug. 1955).

Production of metachromatic colours in solutions of anionic mucopolysaccharides or anionic detergents is accounted for by a theory consisting of four postulates: (1) that chromotropes exist in solution as anionic clusters or micelles, (2) that cations are reversibly bound within such micelles, and are bound more firmly the higher the cationic charge, (3) that the chromotropic micelle selectively and reversibly binds the dye ion of highest charge and so causes shift in the equilibrium of the dye ions in the intermicellar space. Detailed examination of the way in which some dyes deviate from Beer's law supports this theory.
C. O. C.

Structures of Anatase and Rutile. D. T. Cromer and K. Herrington. *J. Amer. Chem. Soc.*, **77**, 4708–4709 (20 Sept. 1955).

Using a Norelco X-ray diffractometer, the crystal structures of anatase and rutile have been determined with greater precision than ever before. For rutile the cell parameters are $a = 4{\cdot}5929 \pm 0{\cdot}0005$ and $c = 2{\cdot}9591 \pm 0{\cdot}0003$ A., for anatase $a = 3{\cdot}785 \pm 0{\cdot}001$ and $c = 9{\cdot}514 \pm 0{\cdot}006$ A. The oxygen parameter for rutile is $0{\cdot}3056 \pm 0{\cdot}0006$ and for anatase $0{\cdot}2066 \pm 0{\cdot}009$. There are four Ti–O distances of $1{\cdot}946 \pm 0{\cdot}003$ A. and two Ti–O distances of $1{\cdot}984 \pm 0{\cdot}004$ A. in rutile. In anatase there are four Ti–O distances of $1{\cdot}937 \pm 0{\cdot}003$ A. and two Ti–O distances of $1{\cdot}964 \pm 0{\cdot}009$ A. Both rutile and anatase contain two elongated Ti–O bonds in each octahedron. These bonds are longest in rutile. This indicates relative weakening of these bonds with consequent lessening of the energy requirements for their excitation. This can be qualitatively correlated with the reflection spectra of the two varieties.
C. O. C.

Pigments in Ancient Japanese Paintings. I. T. Yamazaki. *Proc. Japan. Acad.*, **30**, 781–5 (1954): *Chem. Abs.*, **49**, 11293 (25 Aug. 1955).

Pigments identified as being used on the walls of tombs in A.D. 400–600 are red and yellow ochre, powdered green chlorite rock, white clay, charcoal and pyrolusite. In wall paintings dating from A.D. 600–1800 red ochre, vermillion (cinnabar), red lead, yellow ochre, litharge, malachite, azurite, white clay, $CaCO_3$, and Indian ink were used. On two early scroll paints (A.D. 700–1100) vermillion, red lead, gamboge, malachite, azurite, white lead, Indian ink, gold, silver and an unidentified organic red pigment were used. White lead was apparently too precious to be used on other than scroll paintings.
C. O. C.

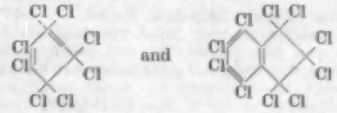
Colour and Constitution of Inorganic Compounds. O. Schmitz-Dumont and B. Raederscheidt. *Naturwissenschaften*, **41**, 477–8 (1954): *Chem. Abs.*, **49**, 10697 (25 Aug. 1955).

If Al in $CoAl_2O_4$ is gradually replaced by Ga, the lattice expands, the strength of the electrostatic field working on Co^{++} decreases, and the light absorption shifts to long wavelengths (curves of spectrum with 3 bands). CoO with In_2O_3 forms only mixed crystals, no spinel. However, Co can replace up to 25 at. % of Mg. in the distilled tetragonal lattice of $MgIn_2O_4$ (inverse spinel). Mg or Co is situated in the octahedral holes and the absorption spectrum is completely different. Co enters isomorphically in Ti (IV) or Sn (IV) spinels of the $Mg^{II}_2\,M^{IV}O_4$ type, so that Co can be found in either tetrahedral or octagonal holes. Up to $Co_{0-4}\,Mg_{1-6}TiO_4$ (or the Sn compound) Co is in the tetrahedral holes, with higher Co content it is mainly in the octahedral holes, and signifies the beginning of the turning from blue to green. With $ZnTiO_4$ up to 10 at. % of Co goes in octahedral holes, thereafter tetrahedral holes are occupied.
C. O. C.

PATENTS

Perchloro-*cyclo*pentene and -indan—Chlorinating Agents. FBy. *BP* 736,436

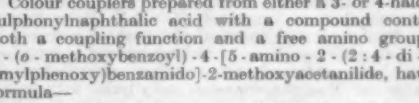
The perchloro compounds—



of pentene and indan respectively combine high-boiling-solvent and chlorinating properties and are useful for chlorinating compounds, e.g. Cu phthalocyanine, which are difficult in the usual solvents, e.g. H_2SO_4 or $ClSO_3H$. They chlorinate by giving up two atoms Cl per mol. and themselves are readily rechlorinated with Cl_2 in presence of $FeCl_3$. The pentene derivative is obtained from aliphatic hydrocarbons with $< C_5$ chain (McBee, *Ind. Eng. Chem.*, **33**, (1941), 181) or from trichloroethylene and carbon tetrachloride (Prins, *Rec. Trav. chim.*, **69**, 1006 (1950)) and the indan from perchlorinated naphthalene (Schwemberger & Gordon, *J. Gen. Chem. U.S.S.R.*, **8**, 1353 (1933)). Copper phthalocyanine is exhaustively chlorinated by heating at 200–300°c. with perchlorindan in presence of $FeCl_3$.
R. K. F.

Colour Couplers. Kodak. *BP* 737,112

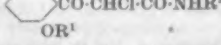
Colour couplers prepared from either a 3- or 4-halogeno-sulphonylnaphthalic acid with a compound containing both a coupling function and a free amino group, e.g. *a*-(*o*-methoxybenzoyl)-4-[5-amino-2-(2:4-di-*tert.*-amylphenoxy)benzamido]-2-methoxyacetanilide, have the formula—



(R = group having a coupling function; X = OH or Hal).
C. O. C.

Colour Couplers. Kodak. *BP* 736,922

Compounds of formula—



(R^1 = Alk, preferably of 1-4 C; R^2 = phenyl substituted in the *m*- or *p*-position), e.g. 4-(*a*-2′-methoxybenzoyl-*a*-chloroacetamido)-3″-(4‴-*tert.*-amylphenoxy)benzanilide, are couplers for yellow dyes. They cause little stain and have high coupling ability.
C. O. C.

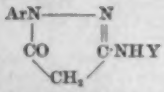
Colour Couplers. Kodak. *BP* 738,138

If the 1-hydroxy-4-arylazo-2-naphthanilide coloured couplers described in *BP* 627,814 (J.S.D.C., **66**, 156 (Feb. 1950)) are substituted in an *ortho* position on the anilide

nucleus they are changed from absorbing more blue than green light to absorbing more green than blue light and so are more clearly the desired magenta. C. O. C.

Pyrazolone Colour Couplers. ICI. *BP* 737,692

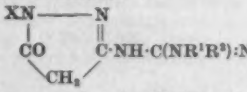
Compounds of formula—



(Y = Alk, aralkyl or *cyclo*alkyl; Ar may be subst.) their enolsulphato derivatives and derivatives having in the 4-position an azo or benzylidene substituent replaceable during colour development, e.g. 1-phenyl-3-benzylamino-5-pyrazolone, are colour couplers which do not yellow on storage or exposure to light. The magenta dyes they yield transmit blue light better than do previously known pyrazolone couplers.

BP 737,700

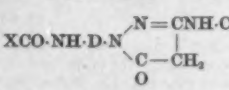
Compounds of formula—



(X = subst. or unsubst. Ar; R^1, R^2 and R^3 = H or subst. or unsubst. Alk or Ar), e.g. 1-phenyl-3-(*N*-phenyl *N'*-benzylguanidino-(*N''*))-5-pyrazolone, have similar properties as colour couplers. C. O. C.

Pyrazolone Colour Couplers. Kodak. *BP* 737,105

Colour couplers having good coupling ability, good solubility and low diffusibility and yielding, in colour development, dye images of good fastness to light have the formula—



(D = subst. or unsubst. *p*-arylene group of the benzene series; X = Ar of the benzene series; Z = Alk or an Ar or aralkyl of the benzene series), e.g. 1-{4'-[3''-(4'''-*tert.* amylphenoxy)-benzamido]-phenyl}-3-[3''-(4'''-*tert.*-amylphenoxy)-benzamido]-5 pyrazolone. C. O. C.

4-Arylazo-5-pyrazolone Colour Couplers. Kodak. *BP* 737,012

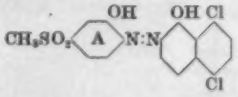
4-Arylazo-5-pyrazolones are produced by treating an aryl diazonium halide with a 4-acyl-5-pyrazolone, a 5-acyloxypyrazole or a 4-acyl-5-acyloxypyrazole. C. O. C.

Sulphobenzamides and Sulphopropionamides as Colour Couplers. Kodak. *BP* 737,103

Colour couplers of formula R·CONH·Y (R = mononuclear 2-sulpho-1-aryl group of the benzene series or a β-sulphoethyl group; Y = a radical having a coupling function) are obtained by treating *o*-sulphobenzoic anhydride or β-sulphopropionic anhydride with compounds of formula NH_2Y, e.g. *o*-aminophenol, 3-amino-5-pyrazolone or α-benzoyl-*p*-aminoacetanilide. C. O. C.

Blue, Metal(Chromium)-complex Monoazo Dyes for Wool, Nylon, etc. Ciba. *BP* 737,189

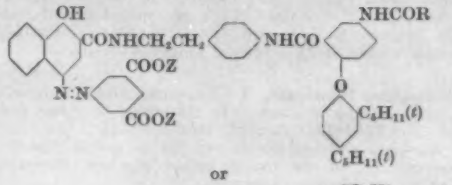
The chromium complexes of monoazo dyes—



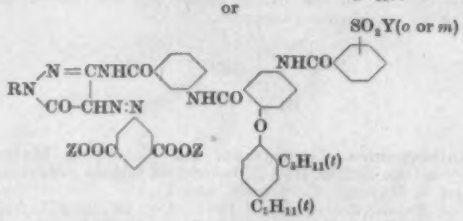
(the nucleus A is free of COOH and SO_3H but may contain Alk, Hal, OAlk, or acylamino, preferably in the 4- or 6-positions) containing < 1, but at least 0·5, Cr atom per mol. of monoazo compound dye wool, nylon, etc. from weakly alkaline, neutral or weakly acid baths. Thus, 1:2-benzoxazolone-5-sulphonyl chloride is reduced to the sulphonic acid by treatment with Na_2SO_3, and methylated e.g. with $(CH_3)_2SO_4$. The oxazolone ring is then split up by means of alkaline hydrolysis, to give 2-aminophenol-5-methyl sulphone. This is diazotised by means of $NaNO_2$ and HCl and coupled in presence of NaOH and Na_2CO_3 with 5:8-dichloro-1-naphthol. The monoazo compound so produced is dissolved in aq. NaOH and treated with sodium chromosalicylate. The water-soluble complex so formed dyes wool full blue from a weakly alkaline, neutral or acetic acid bath. E. S.

Coloured Colour Couplers containing *iso*Phthalic Ester Groups. Kodak. *BP* 737,104

Compounds of formula—



or



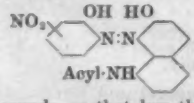
(R = mononuclear Ar; Z = alkali metal or CH_3; Y = OH or arylamido or when Z = alkali metal, Y = OZ) are used as colour couplers which will yield the masking effect described in *BP* 599,377 (J.S.D.C., **34**, 321 (Sept. 1948)) as they retain their original colour in the unexposed portions of the photographic layer. C. O. C.

1:4:5-Trihalogenohydroxyanthraquinone. Interchemical Corpn. *USP* 2,695,302

1:4:5-Trichloro-8-hydroxyanthraquinone is obtained by condensing *p*-chlorophenol with 3:6-dichlorophthalic anhydride in presence of $AlCl_3$. C. O. C.

Metal(Cobalt)-complex Monoazo Dyes for Wool, Nylon, etc. Ciba. *BP* 736,416

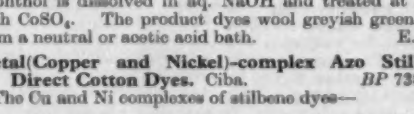
The metal complexes made by treating one or two *oo'*-dihydroxymonoazo compounds free of COOH, SO_3H, and sulphamyl groups—



with cobalt compounds, so that less than 1 atom Co is taken up per mol. of monoazo compound, dye wool, nylon, etc. from neutral or weakly acid baths. Thus the monoazo compound 2-amino-5-nitrophenol → *N*-acetyl-1-amino-7-naphthol is dissolved in aq. NaOH and treated at 80°C. with $CoSO_4$. The product dyes wool greyish green blue from a neutral or acetic acid bath. E. S.

Metal(Copper and Nickel)-complex Azo Stilbene Direct Cotton Dyes. Ciba. *BP* 738,309

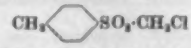
The Cu and Ni complexes of stilbene dyes—



(R^1 = H, Alk or aryl; R^2 = H or Alk; X = OH, OAlk or COOH; R^3 = benzene or naphthalene residue in which the groups X, N:N, and Z occupy respectively the 2, 1, and 4 positions; R^4 = the residue of an azo component introduced by coupling, or a triazol residue formed by oxidising an *o*-aminoazo group; Z = an azo or azoxy link) are direct cotton dyes, generally brown or olive in hue. Thus the monoazo compound 4-amino-4'-nitrostilbene-2:2'-disulphonic acid → phenol is *O*-methylated, and heated in aq. NaOH with the aminoazo compound obtained by reducing the nitroazo compound 2-amino-5-nitroanisole → *N*-*m*-carboxyphenyl-*γ* acid with Na_2S. The product is heated with $CuSO_4$ in presence of NH_3 and ethanolamine to give the copper complex, which dyes cotton khaki. E. S.

Metallisable Monoazo Dyes for Wool, Nylon, etc. Gy. *BP* 737,619

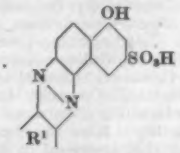
The metal complexes of monoazo dyes containing a chloromethylsulphone group as well as groups (e.g. *o*-carboxy-*o'*-hydroxyazo) capable of metal complex formation, but no SO_3H or additional COOH groups, exhaust more completely on to wool from neutral or weakly acid baths than similar dyes without the chloromethylsulphone group. Thus *p*-toluenesulphinic acid is condensed at 95°C. with dichloroacetic acid under weakly alkaline conditions, with elimination of HCl and CO_2 to give *p*-toluene chloromethylsulphone—



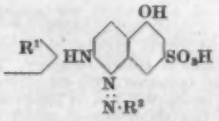
Nitration, reduction, acetylation of the amino group, oxidation of the CH_2 group to COOH, and finally hydrolysis of the acetyl group, give anthranilic acid-4-chloromethyl sulphone. This compound is diazotised and coupled with 1-*m*-chlorophenyl-3-methyl-5-pyrazolone, to give a yellow dye which may be applied to wool by the metachrome process. Its chromium complex is prepared in substance by boiling with ammonium chromosalicylate, and is best mixed with a dispersing agent and trisodium phosphate before use. It dyes wool reddish yellow from a neutral or acetic acid bath. E. S.

Grey, Metal(Copper)-complex, Disazo, Direct Cotton Dyes having an Azine Grouping. S. *BP* 736,180

The copper complexes of azo compounds made by coupling a diazotised 3:3'-dialkoxybenzidine with 1 mol. of an azine—



(R^1 = an aromatic residue), and 1 mol. of a coupling component having an enolisable grouping $-CO\cdot CH_2-$ are grey, direct cotton dyes. Or, instead of the above azine, an azo compound—



(R^2 = benzene or naphthalene series aryl) may be used, ring closure to the azine being effected by acid treatment subsequently. Thus, tetrazotised dianisidine is coupled first with 1 mol. of 5-hydroxy-1:2-naphthophenazine-7-sulphonic acid and then with 1 mol. of 1-(2'-naphthyl)-3-methyl-5-pyrazolone-6':8'-disulphonic acid in presence of pyridine. The disazo compound so formed is boiled with ammoniacal $CuSO_4$ to give the neutral grey copper-complex direct cotton dye. E. S.

Dischargeable Polyazo Direct Cotton Dyes. FBy. *BP* 736,619

Polynuclear aromatic primary diamines, the NH_2 groups of which are separated by >4 C atoms, are condensed with nitroazo compounds by heating in aq. alkaline solutions, preferably containing pyridine. The products are direct cotton dyes of good dischargeability, and may be capable of giving metal complexes if suitable groups are present, e.g. OH and COOH *ortho* to each other. Thus 4:4'-diamino-stilbene-2:2'-disulphonic acid and 4-nitroazobenzene-4'-sulphonic acid are heated together in aq. NaOH containing pyridine. The product dyes cotton yellow–orange. E. S.

Yellow and Brown Azoic Dyes for Terylene. ICI. *BP* 735,119

Arylamides of salicylic acid—

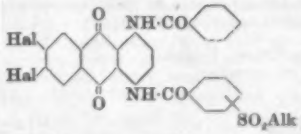
($R = \alpha$- or β-naphthyl, or subst. or unsubst. phenyl; X = H, Hal, or CH_3) may be applied to Terylene along with a diazotisable amine for producing yellow and brown azoic colour on the fibre. Thus salicylanilide is applied to Terylene at 98°C. together with the aminoazo compound formed by coupling diazotised oxalyl-*p*-phenylenediamine with *p*-cresidine and hydrolysing off the oxalyl radical. A reddish brown is then produced by treating with nitrous acid at 85°C. E. S.

1-Acylamino-6:7-dihalogenoanthraquinones—Vat Dyes. Ciba. *BP* 737,016

A 1-amino-6:7-dihalogenoanthraquinone in which at least one halogen is not Cl is acylated with an agent capable of introducing either a *p*-substituted benzoyl radical or a naphthalene-2-carbonyl radical, to give a yellow vat dye. Thus 1-amino-6:7-dibromoanthraquinone is heated with 4-chlorobenzoyl chloride in nitrobenzene for 3 hr. at 130–135°C. R. K. F.

1:4-Dibenzamido-6:7-dihalogenoanthraquinones containing an Alkylsulphonyl Group—Vat Dyes. Ciba. *BP* 736,437

Red vat dyes of formula—



are made by benzoylating a 1-amino-4-benzamido-6:7-dihalogenoanthraquinone so that one of the resulting benzamido groups contains a *m*- or *p*-alkyl-sulphonyl substituent.

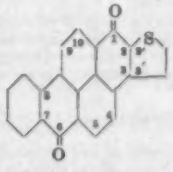
Thus 1-amino-4-benzamido-6:7-dibromoanthraquinone is added to a suspension of 3-methylsulphonyl-benzoic acid in nitrobenzene which has previously been heated at 110–115°C. with $SOCl_2$ and pyridine. The whole is further heated at 125–130°C. for 2 hr. R. K. F.

Bis-(*p*-phenylmercaptophenylamino)-anthraquinones—Neutral-dyeing Acid Dyes. Gy. *BP* 736,187

Anthraquinone derivatives having two replaceable *a*-substituents, e.g. Hal, NO_2, OH or NH_2, are condensed with a 4-aminodiphenyl thioether and then sulphonated to give green neutral dyeing acid dyes for wool and superpolyamides. Thus 4-amino-4'-methyldiphenyl sulphide and 1:4-dihydroxyanthraquinone are heated at 80–90°C. for 30 min. in presence of HCl, while adding Zn dust in small portions. The temperature is raised to 100–110°C. for 24 hr., cooled to 70°C. and butanol added. The resulting crystalline 1:4-bis(4'-*p*-tolylmercapto-anilido)-anthraquinone is filtered off, dried and sulphonated in H_2SO_4 at 15–40°C. R. K. F.

Thienyl-7:8-benzopyrene-1:6-diones—Vat Dyes. Eastman Kodak. *USP* 2,656,361

A 10-methyleneanthrone unsubstituted at 4 and/or 5 is condensed with a thienylvinylketone. The resulting 3-thienoylbenzanthrone is cyclised to the corresponding 2:3-thienyl-7:8-benzopyrene-1:6-dione. The products are yellow to orange hot dyeing vat dyes. Thus 2-thienylvinylketone and 10-methyleneanthrone are refluxed for 5 hr. in acetic acid. The product is cyclised to—



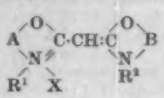
by heating it in a mixture of $AlCl_3$ and NaCl (2:1) containing MnO_2, first at 150–160°C. and then at 185–190°C. for 3 hr. R. K. F.

Dyes for Photographic Light Screens. B. Gaspar, P. D. Dreyfuss, and G. B. Linden. *USP* 2,696,438

Salts of ketimines of formula XYC:NZ (X and Y = *p*-aminoaryl which may be further substituted; Z = subst. or unsubst. hydrocarbon) are useful for dyeing light screening photographic layers. They are stable in alkaline and neutral liquors but readily decolorised in acid baths. Thus 0·01% solution of *N*-phenylauramine in *N*-H_2SO_4 becomes colourless in 2 min. whereas Auramine itself is still coloured after 40 min. C. O. C.

Fluorescent Brightening Agent. Gyv *BP* 736,452

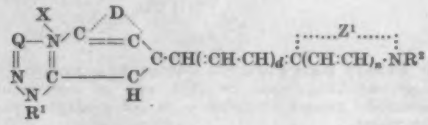
Compounds of formula—



(R^1 and R^2 = Alk and/or alkoxy; X = anion of a strong organic or inorganic acid; A = naphthalene ring linked to the O and N atoms so as to complete a 5-membered ring; B = A or *o*-phenylene), e.g. [3-methyl-(naphtho-1′:2′-4:5)-oxazolo]-[3:5-dimethylbenzooxazolo]-monomethin cyanine *p*-toluene sulphonate, are fluorescent brightening agents particularly applicable to cellulose ester, polyamide and polyurethan fibres. C. O. C.

Cyanine Dyes. Kodak. *BP* 736,266

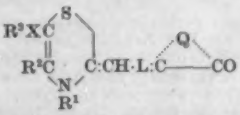
Dyes of formula—



(R^1 or R^2 = Alk or aralkyl; *d* and *n* = 0 or 1; Q = N or methin; D = atoms to complete a benzene ring, which may be substituted; X = acid radical; Z = atom to complete a 5- or 6-membered nucleus), e.g. 1′-3-diethyl-5-*s*-triazolo-(4:3-a)quino-2′-cyanine perchlorate, are useful photographic sensitisers. C. O. C.

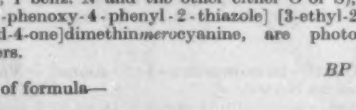
Polymethin Dyes. Kodak. *BP* 738,197

Dyes of formula —



(R^1 = Alk or hydroxy alkyl; R^2 and R^3 = same or different subst. or unsubst. Ar; X = O or S; L = subst. or unsubst. methin; Q = atoms to complete a 5-membered ring 3 benz. C, 1 benz. N and the other either O or S), e.g. [3-ethyl-5-phenoxy-4-phenyl-2-thiazole] [3-ethyl-2-thio-5-thiazolid-4-one]dimethin*mero*cyanine, are photographic sensitisers. *BP* 738,258

Dyes of formula—



(R^1 and R^2 = Alk; R^3 = Alk or hydroxy alkyl; R^4 and R^5 = Ar; X^1 = acid radical; X^2 = O or S; Z = atoms to complete a 5-membered ring), e.g. [3-methyl-5-phenoxy-4-phenol-2-thiazole] [4-(3-ethyl-4:5-benz-2-benzthiazolinyl-idene-ethylidene)-3-methyl-2-thiazol-5-one]methincyanine *p*-toluenesulphonate], are photographic sensitisers. C. O. C.

Carbon Black. Deutsche Gold- und Silber-Scheideanstalt. *BP* 738,068

If the reaction components are supplied as a homogeneous mixture to the flame in the furnace black process, the process can be reliably and economically carried out with good yield of a uniform high grade black. C. O. C.

Dry Pelleting of High-modulus Furnace Black. Phillips Petroleum Co. *USP* 2,695,837

Chromium Oxide Pigments. C. K. Williams & Co. *USP* 2,695,215

Sodium chromate is reduced with sodium sulphide and the resulting mixture of chromium hydroxide and sodium thiosulphate. The mixture is brought to pH < 9 and heated with enough sodium chromate to form with the thiosulphate hydrated oxide of chromium and finally heating at 1650–1950°*F.* to produce chromium oxide. C. O. C.

Iron Oxide Pigments. American Cyanamid Co. *USP* 2,696,426

Transparent yellow (goethite) and red (hematite) crystalline iron oxides are produced by adding to an aqueous solution of a ferrous salt more than its stoichiometrical equivalent of an aqueous solution of an alkali metal carbonate at < 45°c., oxidising at < 45 °c. and then heating the slurry to 80°c. C. O. C.

Isolation and Characterisation of Succinic and Glutaric Acids as *p*-Phenylazoanils (XIV p. 757).

p-Phenylazomaleinanil: A Reagent for Conjugated Dienes (XIV p. 757).

V—PAINTS; ENAMELS; INKS

Pigment Dispersion—Behaviour of Toluidine Red. R. L. Whitney *et al. Paint, Oil and Chem. Rev.*, **117**, (24), 48–50, 52–56 (1954): *Chem. Abs.*, **49**, 5857 (25 April 1955).

Toluidine Red is wetted by Cellosolve and aromatic solvents but not by alkyd, it needs more liquid for wetting out than does TiO_2. Grinding the pigment reduced paste consistency. Best roller mill dispersion of Toluidine Red was obtained with Cellosolve-enriched solvent, low resin content, and a tight setting of the mill. In pebble and steel ball mills low vehicle solids gave most rapid dispersion and best gloss stability. Mass tone colour and tinting strength provide a visual appraisal of dispersion quality beyond limit of fineness of grind gauge. C. O. C.

PATENTS

Improving the Fastness to Light of Coloured Lacquer Coatings. FBy. *BP* 737,385

Incorporation of a urethan containing at least two urethan groups linked by a bridge of > 1 C but free from alcoholic hydroxyl groups considerably improves the fastness to light of colour lacquers. Thus a cellulose lacquer (75 parts) coloured with an alcoholic solution of Astraphloxin FF extra (0·3) has its light fastness improved by addition of the tributylurethan of a tri-*iso*cyanate (25) obtained by treating 3 mol. of toluylene di*iso*cyanate with 1 mol. of trimethylolpropane. C. O. C.

Silver Paint. Erie Resistor Corpn. *USP* 2,695,275

A paint to be fired by heating or firing and which has good electrical conductivity before drying consists of an evaporatable electrically conductive base, e.g. water, a film-forming vehicle, e.g. polyvinyl alcohol, metallic silver and a flux. C. O. C.

Antiseptic Aqueous Vinyl Resin Emulsions. W. H. Engel. *BP* 736,965

Addition of an alkyl thiuram sulphide, e.g. tetramethyl thiuram disulphide, to aqueous vinyl resin emulsions makes coatings formed by them resistant to micro organisms. C. O. C.

Freeze-resistant Aqueous Polymeric Paint. Firestone Tire & Rubber Co. *BP* 738,340–2

VI—FIBRES; YARNS; FABRICS

Chemical Structure and the Useful Properties of Textiles. A. M. Sookne. *Text. Research J.*, **25**, 609–617 (July 1955).

The relationships between the chemical structure of polymers, desirable fibre properties, and desirable end-use properties are discussed. Particular reference is made to the influence of chemical composition upon orientation, crystallinity, and hydrophilic character, and the relationship between these properties and the desirable physical properties of the fibres. W. P. M.

Density of Modified Cottons determined with a Gradient Column. R. S. Orr, L. C. Weiss, H. B. Moore, and J. N. Grant. *Text. Research J.*, **25**, 592–600 (July 1955).

A rapid method for measuring the density of cellulosic materials with a gradient column is described. The column is calibrated by means of coloured glass floats of known density. For measurements on cotton carbon tetrachloride is suitable for the bottom liquid, and a mixture of carbon tetrachloride and a lighter liquid such as xylene is suitable for the less dense liquid. Densities of several cottons before and after chemical modification by partial acetylation, carboxymethylation, aminisation, and mercerisation are given. Percentage acetyl content can be expressed as a function of density in a linear empirical equation over a range of 13–42% acetyl content with an accuracy of $\pm$ 2%. Density measurements of decrystallised, ballmill-ground, and acid-hydrolysed cottons were in agreement with the generally accepted concept of the crystalline–amorphous cellulose phase composition in these materials. Cotton from which water was removed by solvent exchange was found to have a high density before, and a low density after, air drying. This lowered density was attributed to the presence of occluded solvent, which hindered the collapse of the swollen structure. W. P. M.

Textiles with New Properties from Cellulose Triacetate. R. G. Stoll. *Text. Research J.*, **25**, 650–661 (July 1955).

After a brief outline of the historical background, the structure and the fibre properties of cellulose triacetate are correlated with each other and with the characteristics of textiles manufactured from this fibre. The changes in structure brought about by heat treatment are discussed in detail with the aid of photographs of X-ray diffraction patterns and radial X-ray diffractometer curves, and the utilisation of heat treatment for improvement of fibre and fabric properties is described. Brief mention is made of the dyeing of the fibre, stress being laid on the migration of dye from the periphery to the centre of the fibre on heat treatment, resulting in improved fastness properties. Data are given on the durability of triacetate yarns and fabrics when exposed to various service conditions, and are related to the advantageous properties of "ease-of-care" and "wash-and-wear" fabrics and garments. W. P. M.

Physicochemical Observations on the Structure and the Properties of Fully Synthetic Fibres. B. Kramer. *Melliand Textilber.*, **36**, 919–926 (Sept. 1955).

The fibres are considered from the points of view of melting points and ranges, heat and entropy of fusion, and the relations of m.p. to chain length and energy of cohesion. These properties are discussed with specific reference to the chemical constitutions of aliphatic polyesters, polyamides, polyurethans, and aromatic polyesters. S. R. C.

Importance and End-uses of Synthetic Fibres. H. O. R. Kramer. *Textil Praxis*, **10**, 758–764 (Aug. 1955).

Production figures and physical and chemical properties are detailed. The use of blends containing synthetics and their influence on the subsequent properties of the final material are described, together with the end-uses of such materials and the methods of dyeing employed. B. K.

Studies in Pyrolysis. IV—Model Systems for the Pyrolysis of Poly(ethylene Terephthalate) and Allied Polyesters. R. J. P. Allan, R. L. Forman, and P. D. Ritchie. *J.C.S.*, 2717–2725 (Aug. 1955).

Ethylene dibenzoate breaks down in the vapour phase (ca. 400–550°C.) by two competitive routes—(i) a major Alk–O scission to benzoic acid and vinyl benzoate, and (ii) a minor disproportionation to benzoic anhydride and acetaldehyde. The vinyl benzoate formed then pyrolyses by three competitive routes—(i) a major thermal rearrangement to benzoylacetaldehyde, which then undergoes decarbonylation to CO and acetophenone; (ii) a minor Alkenyl–O scission to benzoic acid and acetylene; and (iii) a minor decarboxylation to CO_2 and styrene. Acyl–O scission of vinyl benzoate to benzaldehyde and keten does not occur, but aliphatic vinyl esters (e.g. the acetate and the *iso*butyrate) are pyrolysed not only in like manner to the benzoate but in addition by a major Acyl–O scission to acetaldehyde and a keten corresponding to the acyl group. The bearing of these results on the pyrolysis of cognate polyesters is discussed. H. H. H.

Properties of Acrylic Fibres. E. Schmid and E. Steurer. *Textil Praxis*, **10**, 773–778 (Aug. 1955).

A survey of the physical and chemical properties of acrylic fibres together with methods of dyeing and end-uses of the finished materials. B. K.

PATENTS

Coloured Fibres from Viscose. Courtaulds. *BP* 738,020

The stock colour for adding by injection to the main body of viscose is formed by dispersing a water-insoluble colouring matter in presence of a dispersing agent in an aqueous stable viscous solution of a fibre-forming material, e.g. casein or sodium carboxymethyl cellulose. Such a stock colour remains unaltered for at least a month and so can be made in large batches. C. O. C.

Improving the Dyeing and other Properties of Cellulose Esters. Hercules Powder Co. *BP* 737,224

Treating cellulose esters with a permanganate not only causes cross linking but also distinct improvement in dyeing properties. Cellulose ester fibres so treated have increased ironing points and resistance to dry cleaning solvents and can be dyed with a larger number of wool dyes than are applicable to the untreated fibres. C. O. C.

Rendering Polyvinyl Alcohol Fibres resistant to Boiling Water without Decrease in Affinity for Dyes. Kurashiki Rayon Kabushiki Kaisha. *BP* 737,130

When freshly spun polyvinyl fibres are directly acetylated to render them resistant to boiling water it is necessary to have at least 15% of alkali metal or ammonium salts in the acetylating bath and the affinity for dyes, especially direct dyes, is much decreased. If, however, the softening point of the fibres is first raised to $\geq$ 80°C. (by suitable heat treatment) then they are readily acetylated in a bath containing by wt. 2·8% of formaldehyde or acetaldehyde, 0·5–25·0% of an inorganic acid and 0–5% of an alkali or ammonium salt of an inorganic acid. With the same degree of acetylation in both cases fibres acetylated by the latter process have much greater affinity for dyes. C. O. C.

Water-soluble Alginate Fibres. Courtaulds. *BP* 736,595

Alginate textile materials of desired degrees of solubility are obtained by treating alginic acid with gaseous ammonia or a gaseous lower alkyl amine. W. G. C.

Fibre-forming Linear Polyesters. Rayonier. *BP* 734,800

Low-melting linear polyesters which can be melt-spun to give fibres of good tensile strength are obtained by condensation of the isomers 6- and 7-carboxy-2-hydroxymethyl-1:4-benzodioxane, which are made by condensing epichlorhydrin with protocatechuic acid. W. G. C.

Dyed or Pigmented Filaments, etc. by Melt-spinning Linear High Polymers. V.E.B. Thüringisches Kunstfaserwerk "Wilhelm Pieck" Schwarza. *BP* 737,535

Small amounts of filaments of one colour may be spun uniformly coloured if a mixture is used of (*a*) linear high polymer in which a dye or pigment has been incorporated during polymerisation and (*b*) the same high polymer containing no dye or pigment. C. O. C.

Copolymers of Acrylonitrile and *N*-Vinyllactams. Celanese Corpn. of America. *BP* 736,065

In the preparation of fibre-forming copolymers, hydrolysis of the vinyl lactam is reduced by polymerising in an aqueous medium at pH 5–8 containing dissolved carbon dioxide. W. G. C.

Imparting Increased Affinity for Dyes to Acrylonitrile Polymers. Chemstrand Corpn. *USP* 2,696,483

Copolymers of acrylonitrile and the vinyl alkyl and methalkyl esters of α-halogenocarboxylic acids have their affinity for dyes increased by treatment with a thiourea. C. O. C.

Acrylonitrile Polymer mixed with Formylated Polyvinyl Alcohol—Non-fibrillating Filaments. Eastman Kodak Co. *USP* 2,697,088

Mixtures of 60–90% by weight of polyacrylonitrile and 40–10% of formylated polyvinyl alcohol (polyvinyl alcohol treated with HCOOH to give a product containing 20–37% by wt. of formyl H·CO–) form stable spinning solutions. Fibres spun from such solutions have a higher softening point than polyacrylonitrile–vinyl formate or –polyvinyl acetate fibres and do not tend to fibrillate. C. O. C.

3-Methylenephthalide–Acrylonitrile Interpolymer Fibres. Eastman Kodak Co. *USP* 2,697,092

Interpolymers of 3-methylenephthalide and acrylonitrile are suitable for forming into fibres. C. O. C.

Rough-surfaced Filaments. DuP. *USP* 2,695,835

A plasticised polymer is meltspun into filaments having surfaces considerably more brittle than their cores. The filaments are then drawn 50–200% at a temperature at which their surfaces but not their cores are brittle. Finally the plasticiser is washed out. This results in filaments whose surfaces have a multitude of small cracks which do not however impair the high tensile strength of the filaments. C. O. C.

Textured Pile Fabrics. Alexander Smith. *USP* 2,695,441

Yarn of $>$ 1 ply is twisted tightly and then permanently set preferably while stretched. It is then untwisted, given a loose twist in the opposite direction and given a temporary set, e.g. by light steaming. It is then woven as the pile in a pile fabric. When the pile on the fabric is wetted the pile yarn tends to pull down (cf. *USP* 2,662,558) and coil into a multiple helix with the piles separated and interleaved. C. O. C.

Solutions of Acrylonitrile Polymers (III p. 741).

Origin of Shiny Patches in Worsteds (VIII p. 752).

Differential Dyeing as an Indicator of Bilateral Structure in Wool (XIV p. 758).

Flammability of Fabrics (XIV p. 759).

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Detergency as a Function of Time. M. Rösch. *Melliand Textilber.*, **36**, 58–63 (Jan. 1955).

The major cleansing effect is generally complete after 6–10 min. The best effect in alkaline and neutral wool scouring and in alkaline, neutral, and acid cotton preparation is reached after a more or less constant period. S. R. C.

Properties, Function, and Application of Synthetic Detergents in Textile Processing. H. E. Tschakert. *Z. ges. Textilind.*, **57**, 998–1002 (5 Aug. 1955).

A classification of synthetic detergents based on structure, physical properties, and critical concn. in use. Their function in scouring is discussed under five headings—wettability, emulsifying properties, dispersing properties, ease of removal of soil, and foaming properties. B. K.

Kier Boiling. C. Garrett. J.S.D.C., **71**, 830–839 (Dec. 1955).

The reasons for tendering in kiers are discussed, and the essential conditions to avoid tendering are given. Steam supply is considered, and operational control is described. The importance of fluidity control is stressed. AUTHOR

Present-day Bleaching Practice. N. F. Crowder and W. A. S. White. J.S.D.C., **71**, 764–776 (Dec. 1955).

A general review is given of present practice for bleaching the principal textile fibres, the emphasis being mainly on cotton. Modern trends and developments are discussed, including methods of continuous bleaching and the use of sodium chlorite. Experimental results are quoted in connection with the peroxide bleaching of cotton at various pH values and the application of peroxides for combined desizing, scouring, and bleaching of rayon-staple fabrics. AUTHORS

Accelerated Hypochlorite Bleaching of Cotton. R. L. Derry. J.S.D.C., **71**, 884–893 (Dec. 1955).

An attempt is made to determine the conditions under which warm or hot hypochlorite solutions can safely be used in cotton bleaching. It is shown that alkaline hypochlorite liquors, buffered at pH 10·5 or above, are very stable even on boiling. If the time of bleaching is reduced by a factor of 2·3 for each 10°C. rise in temperature, the quality of the bleach is maintained without appreciable increase in the extent of modification of the cellulose. AUTHOR

Bleaching of Nylon and Nylon Blends. S. Shaw and W. S. Willson. J.S.D.C., **71**, 857–873 (Dec. 1955).

The effect of chemical bleaching agents on the strength and colour of all-nylon textiles, and on the tensile strength and abrasion resistance of wool–nylon, cotton–nylon, and staple viscose–nylon blended fabrics has been investigated. In addition, methods of bleaching a cotton–nylon blended fabric to give an acceptable white have been described. Removal of heat-setting discoloration from all-nylon material has been discussed, and also the use and misuse of fluorescent brightening agents. The bleaching agents selected for investigation were sodium hypochlorite, hydrogen peroxide, peracetic acid, and sodium chlorite, and details are given of recommended methods of application. AUTHORS

PATENTS

Bleaching Cellulose Pulp. Tennants Consolidated. *BP* 736,541

In a multi-stage process sulphite pulp is given a preliminary partial bleach in aqueous medium in which 50–60% of the chlorine demand of the pulp (determined by the permanganate number) is supplied by a chlorite and hypochlorite at pH 2·5–2·7, bleaching being completed with aqueous hypochlorite. Of the chlorine requirement in the preliminary bleach 50–75% is supplied by the chlorite. S. V. S.

Continuous Scouring of Cotton. Johnson & Johnson. *BP* 737,078

Raw cotton is finely dispersed in an air stream and deposited on a conveyor, e.g. a rotating drum, to give an even layer of weight $>$ 3 grains/sq.in. It is allowed to fall thence down a tube containing baffle plates which ensure a zig-zag course and from the top edge of which is sprayed caustic soda solution (2–5% strength) at about 190°F. and containing a wetting agent. This violently agitates the cotton and makes for effective purification. The fibres pass into a tank which permits the time of treatment to be suitably extended and are then drained, sprayed with water, and conveyed into a bleach tank, passing through this in a suitable time, from which they are conveyed through acidifying and washing sprays. The machine can be used for continuous treatments other than scouring. J. W. B.

Bleaching Textiles with Chlorites. FBy. *BP* 734,732

The materials are impregnated with a neutral aqueous solution containing 1–10% of an alkali metal or alkaline earth metal chlorite, excess liquor removed, and the material finally treated for $>$ 15 min. with steam at 110–140°C. There is no degradation of the fibre. If desired, the process can be combined with setting of polyamide or polyacrylonitrile fibre materials. C. O. C.

Treating Vegetable Fibrous Materials with Gaseous Chlorine or Chlorine Dioxide. Cellulose Development Corpn. *BP* 736,491

Vegetable fibre pulp is treated with gaseous chlorine or chlorine dioxide by causing the pulp to descend through two zones on an apparatus and being treated in two stages, one for each zone. In the first stage the pulp is treated with gaseous chlorine or chlorine dioxide for 10–45 min. at a consistency of 10–40% and in the second stage it is diluted and agitated with fresh water or used acid water to bring the consistency to $<$ 10% and treatment with chlorine or chlorine dioxide continued for up to 1 hr. with or without addition of further gaseous chlorine or chlorine dioxide. The course of the first stage treatment is observed through windows in the apparatus. The quantity of chlorine used produces an acidity of from 10–40 g. of HCl per litre of water present during the greater part of the

first stage. The first stage may be carried out in parallel for two or more towers with a chlorine-resisting lining and a machine for opening out the consolidated fibres is provided before introduction into the towers which are 21–36 in. internal diameter and 10–45 ft. high.
S. V. S.

Solvent Scouring Wool. Distillers Co. *BP* 738,014
Raw wool is washed with a polyhydric alcohol or a keto alcohol containing > 3 C, e.g. hexylene glycol, 2-methyl pentan-2:4-diol, or diacetone alcohol, at 50–60°c. Both wax and suint are removed to about the same extent as in aqueous scouring but the handle of the wool is greatly superior.
J. W. B.

Decolourising Cellulose Ethers. Hercules Powder Co. *BP* 736,304
Water-soluble cellulose ethers, e.g. carboxy-methyl cellulose, are decolourised by treating with an organic liquid, e.g. methanol, containing a water-soluble inorganic chlorite, e.g. sodium chlorite, at < pH 6, or sodium chlorite and hypochlorite at > pH 6.
W. G. C.

Dry-cleaning and Weatherproofing Fabrics. Emery Industries. *USP* 2,695,250
The surface active agents employed in dry cleaning solvents impair any water repellent finish which is on the goods or may be applied to them after dry cleaning. The deleterious effect of such agents retained by the goods can be nullified by impregnating the goods with a metallic salt of the type of aluminium acetate or an alcoholate of the type of aluminium propoxide. Preferably the dry cleaned fabric is rinsed in a dry cleaning solvent containing an aqueous dispersion of stearic amine acetate made by use of a cationic emulsifying agent.
C. O. C.

Control of Appearance Changes due to Soiling—Mechanism, Measurement, and Reduction of Soiling Changes in Carpets during Use (X p. 755).

VIII— DYEING

Daylight Fading compared in Different Parts of France. J.-P. Niederhauser. *Teintex*, **20**, 673–679 (Sept. 1955).
Eight blue wool dyes were compared under E.C.E. conditions at six different fading stations situated in the Departments of Oise, Seine, Isère, Gard, Maritime Alps, and Eastern Pyrenees. The degrees of fading were correlated with the times of sunlight exposure. The rate of fading was markedly greater in the South than in the Paris region, whilst the mountainous regions showed even more rapid fades.
S. R. C.

Dyeing of Viscose Rayon Cakes with Direct Cotton Dyes. T. Flanagan. J.S.D.C., **71**, 790–796 (Dec. 1955).
The various classifications of direct cotton dyes according to their dyeing behaviour are reviewed with reference to their assistance to the viscose rayon cake dyer in his choice of dyes. The interpretation of the graphical data of the dyeing characteristics of direct dyes and its limitations are discussed with particular reference to the value of this system in the selection of dyes for cake dyeing and the formulation of a suitable dyeing method.
Some reference is also made to the advantages and limitations of high-temperature dyeing using pressurised machines.
Author

Pad–Roll Dyeing System. C. O. Eriksson, N. Landqvist, and B. Mellbin. J.S.D.C., **71**, 894–901 (Dec. 1955).
A brief discussion is given of the Pad–Roll system. The dyeing machine, comprising a padding device, an infrared heating zone, and a batching chamber in which constant atmospheric conditions can be maintained, is described. The composition of the direct dye pad solutions is discussed with special reference to dyes and addition of electrolytes, and the pre- and after-treatments of the fabrics are considered. Finally, the laboratory dyeing methods applicable to the Pad–Roll system are given.
Authors

Continuous Dyeing of Cellulose Fabrics with Direct Cotton Dyes. J. Wegmann. J.S.D.C., **71**, 777–789 (Dec. 1955).
There are two main reasons why direct cotton dyes are difficult to apply by continuous methods. Firstly, it is difficult to maintain uniformity of colour during the dyeing process because of the affinity of the dye for the fibre. Secondly, direct cotton dyes of good wet fastness have a low rate of diffusion, which means that a longer steaming time is necessary to bring about fixation. It has been found that copper-complex polyazo dyes form loose complexes with certain amines, and that these complexes diffuse rapidly and can be applied evenly to the fibre. These amines are displaced during steam fixation in an ager and are subsequently removed by rinsing, which results in a normal dyeing. This method also permits simple and reliable continuous application of highly substantive direct dyes, such as are to be found in the range of copper-complex products.
Author

High-temperature Dyeing of Cellulosic Fibres. A. Schmitz. J.S.D.C., **71**, 910–917 (Dec. 1955).
The fundamental principles determining the effect of elevated temperature on the substantivity, the rate of dyeing, and the levelling power of direct dyes are discussed with the aid of exhaustion curves. Since less dye is absorbed above 100°c. than at normal dyeing temperatures, dyeing should be continued in a cooling dyebath after the high-temperature stage. Although the equilibrium concentration of dye on the fibre is attained more rapidly at higher temperatures, the amount of dye absorbed in unit time is lower, provided that the dye liquor has free access to the fibre. Reasons for the more rapid dyeing observed in practice are better levelling power and reduced swelling: at lower temperatures swelling tends to constrict the interstices between the individual fibres, through which liquor can flow. An explanation is given for the surprising fact that the increase in levelling power produced by a given rise in temperature does not depend on its value at the lower temperature. Vat dyes and synthetic fibres are considered briefly.
C. J. W. H.

Service Fading of Disperse Dyes by Chemical Agents other than the Oxides of Nitrogen. V. S. Salvin and R. A. Walker. *Text. Research. J.*, **25**, 571–585 (July 1955).
An extensive trial of acetate rayon fabrics dyed with new "gas-fast" blues has shown that active agents in the atmosphere, in addition to the oxides of nitrogen, can cause fading in service. This fading is oxidative in nature. It has been reproduced by an accelerated laboratory test in which fabrics have been exposed to concentrations of ozone somewhat higher than those ordinarily found in the atmosphere. This type of fading has been designated "O-fading". All the blue disperse dyes and some of the reds and yellows have been found to be subject to O-fading; but the major problem is with the blues. Anthraquinone blues are bleached by O-fading without the reddening associated with gas-fume fading. O-Fading can be inhibited by antioxidants such as the gas-fume fading inhibitor diphenylethylenediamine and the non-gas-fume fading inhibitor *p*-octylphenol. For optimum resistance to both forms of atmospheric fading, acetate rayon fabrics dyed with disperse blues, including gas-fume-fast blues, should be processed with inhibitors.
Laboratory tests have shown that O-fading takes place on Dacron (polyethylene terephthate) as well as on secondary acetate and Arnel (cellulose triacetate). With Arnel and Dacron a marked increase in resistance is obtained on heat treatment. The penetration of the dye into the fibre is a factor in O-fading behaviour, as evidenced by the increase in resistance to O-fading of Dacron fabrics dyed with the aid of a carrier and by the effect of heat treatment. Optimum resistance to atmospheric fading of Arnel is obtained by use of inhibitor plus heat treatment.
W. P. M.

Dyeing and Finishing of Cellulose Triacetate Yarns and Fabrics. A. Mellor and H. C. Olpin. J.S.D.C., **71**, 817–829 (Dec. 1955).
The physical and textile properties of cellulose triacetate fibres are such that fabrics made from them, or containing substantial proportions of them, may be permanently set in much the same way as are nylon and Terylene. The

dyeing properties of triacetate yarns are compared with those of secondary acetate yarns, both alone and in admixturewith other fibres. AUTHORS

Theory of Wool Dyeing. II—The Kinetic Approach. L. Peters. J.S.D.C., **71**, 725–732 (Dec. 1955).

Dyeing of Protein and Polyamide Fibres with 1 : 2 Metal Complexes. F. Weber. *Textil Praxis*, **10**, 825–828 (Aug. 1955).

A study of the dyeing rates of representative 1 : 2 metal complexes in the Cibalan and Irgalan ranges under varying dyeing conditions, including hard water. B. K.

Wool Damage in Different Dyeing Processes—II. A. Würz. *Melliand Textilber.*, **36**, 931–938 (Sept. 1955).

Wool dyeing with normal dyeing times is not attended with danger if suitable dyeing methods are used, e.g. pH control and auxiliaries. Longer times are more harmful the further the pH of the dyebath is from 3·5–4. This factor is of increased importance where prolonged shading, or stripping and redyeing, is involved. S. R. C.

Origin of Shiny Patches in Worsteds. H. Reumuth. *Textil Praxis*, **19**, 635–640 (July 1955).

The causes of shiny patches in worsteds during wear are discussed, and the effect on fibre structure is examined with the aid of photomicrography. B. K.

Recent Progress in the Dyeing of Terylene Polyester Fibre. A. S. Fern and H. R. Hadfield. J.S.D.C., **71**, 840–856 (Dec. 1955).

The first part of this paper summarises existing knowledge of the dyeing of polyester fibres, and indicates how the main developments in dye application have taken place. The second part describes mainly unpublished work on Terylene polyester fibre concerned with the application of azoic dyes and the dyeing of blends of Terylene with wool. AUTHORS

Difficulties in Stripping Orlon dyed by the Cuprous Ion Technique. D. R. Sharma and K. S. Campbell. *Text. Research. J.*, **25**, 602 (July 1955).

Usually Orlon dyed by the cuprous ion technique can be stripped by successive treatments with acidified sodium chlorite. A considerable portion of copper remains in the fibre after the dye has been removed. When the fibre is redyed above 212°F. the colour is dull or brown; in fact, the fibre turns brown in the absence of dye when held at 230°F. in water for 30 min. Steam or dry heat treatment gives the same result. This discoloration was prevented reasonably effectively by treating the dyed fibre with synthetically prepared sodium salts of polyamine acids and then with sodium chlorite in the presence of nitric acid. W. P. M.

Treating Vinylon with Aromatic Amino Aldehydes before dyeing with Azoic Dyes. N. Kuroki, K. Wakamatsu, F. Konishi, and K. Konishi. *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **57**, 870–3 (1954): *Chem. Abs.*, **49**, 10628 (10 Aug. 1955).

Vinylon (a polyvinyl alcohol fibre with various degrees (32·5–48·4%) of formalisation) was treated at 60–75°C. for various periods up to 3 hr. with *p*-aminobenzaldehyde or *p*-dimethylaminobenzaldehyde in presence of H_2SO_4 and Na_2SO_4. Data on the variation of the degree of formalisation, N content, etc. are given. The treated fibres dyed with various azoic dyes yielded browns of good fastness to light, washing, and rubbing. C. O. C.

Dyeing Vinylon Black with Oxidation Dyes—II. Y. Hamasaki and T. Urahata. *Science & Ind.* (Japan), **27**, 139–146 (1953): *Chem. Abs.*, **49**, 12007 (10 Sept. 1955).

p-Phenylenediamine gave the darkest dyeing followed by the *m*- and *o*- in that order. Further substitution in the *p*-position deepened the colour. Introduction of OH facilitated oxidation but had little effect on colour. In presence of phenol or aniline the *p*-substituents again yielded the darkest colour. Increase in pH led to proportionate increase in the depth of the dyeings. Presence of OH, *p*-NH_2 and NH_2 groups had a deleterious effect on fastness. C. O. C.

Ultrasonic Tanning and Dyeing. F. Gutman. *J. Br. Inst. Radio Eng.*, **15**, 357–364 (July 1955).

A review of work done on the application of ultrasonics to the dyeing of textiles and the tanning of leather. Similarities and dissimilarities of both processes are discussed in the light of the physico-chemical processes involved. The increase in ultrasonic power required for industrial use is estimated. These power requirements cannot be met by crystal transducers and it is therefore suggested that the operating frequency be reduced to the higher sonic or low ultrasonic range so as to permit use of magnetostrictive devices. Effectiveness of sound at low and high frequencies are compared. Some sources of high ultrasonic power are described. 37 references. C. O. C.

PATENTS

Fugitive Tinting of Textiles. BrC. *BP* 737,886

Very satisfactory tinting is obtained by using a direct dye in presence of a water-soluble addition polymer of an *N*-vinyl lactam, particularly of *N*-vinyl pyrrolidone. Thus cellulose acetate staple fibre is satisfactorily tinted by moistening it with an aqueous solution of Chlorazol Fast Pink BKS (1 g. per litre) and Albigen A (polyvinylpyrrolidone) (4 g. per litre). The sighting colour is readily removed by a mild soap scour even after the tinted fibres have been steamed for 15 min. at 220°F. C. O. C.

Tetrabenzylmethylenediamine as Gas Fume Fading Inhibitor. Celanese Corpn. of America. *BP* 736,173

Tetrabenzyl-methylene diamine is an excellent gas fume fading inhibitor, 1–3% on the weight of cellulose acetate giving the best results. It can be applied in the dyebath or may be incorporated in the fibre during spinning. C. O. C.

Alkylated Polyamines for imparting Improved Fastness to Wet Processing to Direct Dyes. FBy. *BP* 736,914

β-Halogeno ethylene amines or their salts are treated with an alkali metal hydroxide in a solvent at pH 7–12, if desired in presence of alkylene diamines or polyalkylene polyamines. The resulting polyamines are then alkylated. The products impart better wet fastness to direct dyeings than either the alkylated polyamines prepared by the methods described in *BP* 435,388 (J.S.D.C., **52**, 187 (April 1936)) or the alkylated polymerised ethylene imines described in *BP* 416,354, probably because the former are below the optimum mol. wt. for this purpose, while the latter exceed it. C. O. C.

Condensates of Complex Copper Compounds with Nitrogenous Compounds and Aldehydes. FBy. *BP* 736,792

A nitrogen-containing complex copper compound, e.g. bis-(diethylene triamine)-copper chloride, is condensed with a compound containing at least one

group, e.g. dicyandiamide and a low mol. wt. aldehyde, e.g. HCHO. The product improves the wet fastness and the fastness to light of direct dyes on cellulose. C. O. C.

High-temperature Vat Dyeing. American Cyanamid Co. *BP* 734,531

Addition to the vat of an ionisable Mg and/or Mn compound and/or trialkanolamine prevents excessive consumption of hydrosulphite when dyeing with vat dyes at high temperatures. There should be at least 0·001 mol. of Mg ions or 0·0005 mol. of Mn ions or 0·001 mol. of trialkanolamine per mol. of hydrosulphite. Thus to a liquor (200) containing *C.I.* 1113 (0·5), NaOH (6) and $NaNO_3$ (1·5) was added $MgSO_4{\cdot}7H_2O$ (0·25). It was brought to 200°F. and sodium hydrosulphite (6) added. After fifty minutes the bath still contained 2·2 parts of sodium hydrosulphite, whereas a similar bath containing no Mg salt contained $< 0{\cdot}7$ parts of hydrosulphite after only 20 min. C. O. C.

Dyeing Cellulose Acetate with Vat Dyes. Celanese Corpn. of America. *BP* 735,396

The material is treated with an aqueous dispersion of the vat acid containing polyvinyl pyrrolidone and then oxidised. This gives well penetrated dyeings, of good colour value and fast to rubbing. C. O. C.

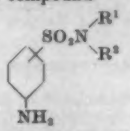
Vat Dyeing of Acrylic Fibres. General Aniline. *USP* 2,695,832

The material is impregnated with an acidified vat (i.e. an aqueous alkaline vat acidified in presence of a dispersing agent), dried and then heated for a little time. The resultant dyeings can be of any desired depth and have excellent fastness to light, washing, and rubbing.

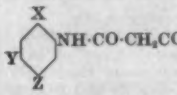
C. O. C.

Yellow Azoic Dyeings on Cellulose Acetate, Superpolyamides and Polyurethans. FH. *BP* 737,270

Fast yellows on cellulose acetate, superpolyamide and polyurethan fibres are produced by treating in a solution containing an amino compound—



(R^1 = H or Alk; R^2 = Alk, Aralk or a hydroaromatic radical) which may be further substituted by alkyl, alkoxy or aryloxy, and the alkali metal salt of an acylacetic acid arylamide—



(R^3 = Alk or phenyl; X = Alk or Alk·O; Y = Alk·O or Hal; Z = Alk or Alk$_2$O); diazotising in a nitrous acid bath and finally developing in a hot bath. Thus cellulose acetate is treated for 1–1·5 hr. at 75°C. in a bath containing the Na salt of 1-acetoacetylamino-2:5-dimethoxy-4-chlorobenzene and 1-amino-2:5-dimethoxy benzene-4-sulphon-*N*-ethyl-cyclohexylamide containing diethanolamine, the condensation product of oleyl chloride and lysolbic acid (cf. *BP* 413,016, J.S.D.C., **50**, 370 (Nov. 1934)) and NaCl. Diazotisation is effected in cold bath of $NaNO_2$ and HCl, and the dyeing finally developed at 60–80°C. in a solution of oleylmethyltaurine containing sodium acetate and ammonia.

R. K. F.

Striped Patterns on Textile Fabric. Springs Cotton Mills. *BP* 734,528

The fabric in open width is treated longitudinally with several separated streams of a freely-flowing aqueous striping solution, running warpwise of the moving fabric. The whole of the fabric is then immediately saturated with a second freely-flowing aqueous solution that prevents migration of the first solution. One of the solutions consists of a dye liquor and the other consists either of a differently coloured dye liquor or a dye resist solution. Thus cloth passes at 100 yd. per min. over a series of driven, separated wheels or discs having a surface speed of 35 yd. per min. and which rotate in a bath made up of water (10 gal.) and Na alginate (8 oz.) at 100°C. Immediately it has passed over the wheels the fabric passes into a two roll padder, working at six tons pressure, where it is treated with an aqueous solution at 120°F. containing per 100 gal. Cibanone Brown BGN double paste (2·9 lb.), Indanthrene Brown RAP paste (0·9), Indanthrene Brown BRA paste (0·1), caustic soda 50% (12) and sodium hydrosulphite (6). Finally it passes through a series of units for reduction, rinsing, oxidation, and soaping. *BP* 734,542

The striping liquor is applied from an applicator roll combined with the pad, this applicator roll being driven independently of the operating speed of the pad.

C. O. C.

Severe Pitting of Stainless (18–8) Steel in Hot Chloride Dyebaths (I p. 738).

The Irgalan Dyes— Neutral-dyeing Metal-complex Dyes (IV p. 742).

Yellow and Brown Azoic Dyes for Terylene (IV p. 747).

Coloured Fibres from Viscose (VI p. 749).

Synthetic Resin Coating Compositions (IX this page).

Differential Dyeing as an Indicator of Bilateral Structure in Wool (XIV p. 758).

IX— PRINTING

Fixation of Disperse Dyes on Printed Polyester Fabrics. R. Zeidler. *Textil Praxis*, **10**, 820–824 (Aug. 1955).

The use is described of carriers, high-pressure steaming, and heat treatment on the lines of the Thermosol process for the fixation of prints of disperse dyes on polyester fibres.

B. K.

Recent Progress in the Diazotype Process. II. Modern Couplers; Processes actually used. L. Mester. *Science et inds. phot.*, **26**, 249–259 (1955): *Chem. Abs.*, **49**, 11473 (10 Sept. 1955).

Review, 35 references.

C. O. C.

Subtractive Colour Reproduction: Evaluation of the Actual Colour-reproduction Equations for a Colour Process. W. R. J. Brown. *J. Opt. Soc. Amer.*, **45**, 539–546 (1955): *Chem. Abs.*, **49**, 10774 (25 Aug. 1955).

The requirements for a photographic system to reproduce the chromaticities of selected colours can be described by a set of equations. These equations relate the amounts of dye needed in the reproduction to the exposure ds. of the original colours. Such equations are given for a negative-positive colour system. They state the requirements to be met by a colour system if it is to reproduce the chromaticities of the original. A similar set of colour-reproduction equations can be worked out to describe the actual performance of the colour system. These actual colour-reproduction equations are established by measuring the actual amount of dye produced when reproducing a colour chart. These amounts of dye are related to the exposure ds. of the original colours. The required and actual colour-reproduction equations for a negative-positive colour system are compared. The similarity between the two sets shows how well a modern negative-positive colour system fulfils conditions of good colour reproduction.

C. O. C.

Subtractive Colour Photography: Spectral Sensitivities and Masks. W. T. Hanson and W. L. Brewer. *J. Optical Soc. Am.*, **45**, 476–481 (1955).

Colour Correction in the Agfacolor Negative–Positive Process by use of Coloured Masks. E. Hellmig. *Phot. Korr.*, **91**, 51–8 (1955): *Chem. Abs.*, **49**, 10106 (10 Aug. 1955).

The basic principles of correcting for unwanted adsorptions of the image dyes in subtractive colour processes by use of colour masks are described with the aid of colour plates. Preparation of a separate yellow dye mask to compensate for the blue absorption of the magenta dye in the Agfacolor negative film is described.

C. O. C.

PATENTS

Printing Screens. J. B. Brennan. *BP* 737,084

One or more layers of unwoven parallel filaments of durable material, e.g. metal, have the spaces between them blocked by an imperforate layer of another durable material, e.g. thermosetting plastic or a metal different from the filaments. The design is formed by removing appropriate portions of the imperforate layer. Such screens are insensitive to atmospheric changes, wear well and are flatter than woven screens.

C. O. C.

Alginates for Thickening Agents for Vat Dye Printing Pastes. A/S Protan. *BP* 734,627

An aqueous solution of Na alginate is heated to 60–100°C. and dry K_2CO_3 added and the mixture stirred for 5–60 min. at $\not< 70$°C. It is then cooled to < 50°C. and dye and reducing agent stirred in until a homogeneous paste is obtained.

C. O. C.

Synthetic Resin Coating Compositions. Fred'k H. Levey Co. *BP* 735,051

Coatings which do not require high temperatures for curing consist of an aqueous emulsion of an organophilic thermoplastic resin and a basic salt of a carboxylic copolymer of styrene and an acid ester of a polymerisable polycarboxylic acid. They may or may not be pigmented and are particularly suitable for the coating or printing of textile fabrics, the resin being set by passing the coated or printed fabric, preferably while the coating or print is still wet, into either an acid or an alkaline bath, curing being effected during normal drying.

BP 735,234

Colour migration is prevented and the use of an aqueous bath avoided by setting the coatings or prints by exposing the coated or printed fabric to an acid vapour and then curing at 115–150°C. C. O. C.

Heat-reflective Fabrics. American Cyanamid Co. *USP* 2,695,895

A leafing metal powder is printed onto the fabric using as the carrier and adhesive a urea or triazine resin formed by condensation with an aldehyde in presence of an aliphatic primary alcohol of 4–8 C, e.g. a butylated melamine-(or urea-) formaldehyde resin. The resin is plasticised with an alkyd resin and dissolved in an organic solvent and then formed into a water-in-oil emulsion to form the printing composition. The resin : pigment ratio is preferably 1:1. Fabric printed with such a composition has the following properties: (1) Infra-red transmission 10% of that of the uncoated fabric, (2) good handle and flexibility, (3) no strike-through, (4) negligibly affected by dry cleaning, (5) good resistance to rubbing, (6) light weight, about 2·5 g. of metal pigment per sq. yd. C. O. C.

Improving the Printing Properties of Polyethylene. DuP. *BP* 738,474

Adhesion of printing inks, e.g. photogravure or aniline inks, is much improved if the polyethylene is pretreated with ozone at 150–325°C. in presence of a halogen, hydrogen halide or nitrous and preferably in presence of ultraviolet radiation. C. O. C.

Multicoloured Coating of Sheet Material. Tobey Color Card Co. *USP* 2,695,005

A method of producing colour charts, paint pattern cards, etc. C. O. C.

Depositing Paint and other Viscous Materials. McCorquodale Colour Display. *BP* 736,963

In printing several colours with a matrix containing recesses to hold the colour to be printed, means are provided to remove the air from the recesses so that they become completely filled with colour. This gives great precision as to the amount of paint, etc. applied from each recess. C. O. C.

Recording by Decolorising. National Cash Register Co. *USP* 2,695,245

The whole recording area of a base material is coloured by combining two substances on it, e.g. white paper is coated with particles of an adsorbent material which acts as an acid, e.g. attapulgite, and is then treated with Crystal Violet lactone. The record is then made by applying a liquid which decolorises the Crystal Violet, e.g. an alcoholic solution of stearyltrimethylammonium chloride $C_{18}H_{37}{\cdot}N(CH_3)_3Cl$. C. O. C.

Colour Photography. Ciba. *BP* 738,233

A dye image can be produced in place of a silver image in a photograph by using a photographic layer free from insoluble silver salts and developing it in presence of a colour coupler, e.g. 1-hydroxy-2-naphthoic acid anilide, and a soluble reducible silver or mercury salt with an amine suitable for colour formation, e.g. 2-amino-5-diethylamine toluene hydrochloride. C. O. C.

Rapid Development of Exposed Layers of Rotary Photogravure Tissues sensitised with Diazo or Azide Compounds. Powers Chemco. *USP* 2,695,846

Black Printers for use in Four-colour Photomechanical Printing and Electro-optical Methods for making them. Eastman Kodak Co. *BP* 736,864

Preparing Stereotype, Electrotype, Plastic or other Plates for Colour Printing. R. B. Production & Engineering Co. *BP* 736,002

Method and apparatus for obtaining accurate registration of duplicate printing colour plates. C. O. C.

Mixed-grain Colour Photography. Kodak. *BP* 736,228

Modification of *BP* 702,200 (J.S.D.C., **70**, 135 (March 1954)) to enable a three colour material to be used in which the three emulsions are all silver bromide or all silver bromoiodide and no yellow filter dye is used. C. O. C.

Colour Correction for Separation Negatives or Positives for use in Colour Reproduction. J. F. Crosfield. *BP* 737,768

BP 738,118

Stain Removal in Colour Photography. Agfa AG. für Photofabrikation. *BP* 736,881

Furoquinoxalines and Thienoquinoxalines as Accelerators for Dye Bleach Baths for Colour Photography. General Aniline. *BP* 736,849

Photomechanical Reproduction Materials. Kalle & Co. *BP* 737,379

A support has a hydrophobic surface which when saponified becomes hydrophilic. A light-sensitive coating applied to this surface contains a light-sensitive, water-insoluble, alkali-insoluble quinone diazide which when exposed to light becomes soluble in alkali. Printing plates are formed by exposing such a material to light and then treating with an aqueous saponifying agent. C. O. C.

Screen Printing. Stoffer & Co. *BP* 738,349

The fabric to be printed is bonded to an endless conveyor and intermittently fed in steps of at least two repeat lengths between one or more stationary printing tables with their respective stencils and then through a drying chamber. C. O. C.

Flock Prints and Panne Effects. Velveray Corpn. *USP* 2,696,445

Adhesive and flock are successively applied with or without a roller printing design. The flock is partly set and then flattened or panned (to produce a "panne" effect) between rubber blankets under sufficient pressure to assure the desired alignment of the flock without weakening or distorting adhesion between the flock and the backing. C. O. C.

Printing or Decorating Ceramic Ware (I p. 739).
Striped Patterns on Textile Fabric (VIII p. 753).
Factors influencing Emulsion Stability and Viscosity (XV p. 760).

X— SIZING AND FINISHING

Raising of Textile Fabrics. C. S. Whewell. J.S.D.C., **71**, 902–909 (Dec. 1955).

Methods of assessing the effectiveness of raising are discussed, and these are used to express quantitatively the part played by cloth construction and conditions of raising (pH, presence of lubricants and salts, etc.) in determining the response of a fabric to raising. Emphasis is laid on changes in thickness, tensile strength, and pile composition produced during raising. AUTHOR

Condensation of Urea and Formaldehyde on Cellulosic Materials. J. Alvsaker and H. A. Turner. J.S.D.C., **71**, 797–816 (Dec. 1955).

Experiments have been carried out in which the drying and high-temperature treatments of viscose rayon, impregnated with urea–formaldehyde precondensates, have taken place both in ventilated and in closed vessels. In this way the condensation has been effected with different concentrations of formaldehyde vapour in the surrounding air. These variations in the post-impregnation treatments affect the following quantities—proportion of resin fixed, fastness of the resin to removal by washing, crease resistance, stiffness, tensile strength, extension at break, and water retention. The relations between conditions of treatment and corresponding changes in the properties of the treated materials are discussed. AUTHORS

Rotproofing of Viscose Rayon. I—Treatment of Viscose Rayon with Formaldehyde and Formaldehyde-containing Resins. J. W. Bell, M. M. Ramsey, and C. S. Whewell. J.S.D.C., **71**, 660–667 (Nov. 1955).

Viscose rayon yarn is treated with formaldehyde and a number of formaldehyde-containing resins in an attempt to obtain a rotproof finish. The most outstanding result

which emerges from the experiments is that halogenated phenoplasts are more efficient than either urea–formaldehyde or phenol–formaldehyde and that a resin prepared from bromophenol and formaldehyde is exceedingly effective, a deposit of only 5% on the yarn being resistant to microorganisms under the most severe and prolonged test conditions. It also appears possible to improve the efficiency of urea–formaldehyde resin by incorporating a small proportion of halogenated resin.

Urea–formaldehyde resin by itself is effective only if present in prohibitively high concentrations; below 15–20% the proof breaks down on prolonged testing. Formaldehyde alone is moderately effective, and appears to have little effect on the wet tensile strength of the viscose rayon; it may be of value where conditions highly favourable to the growth of microorganisms are not likely to be encountered.

The experiments have shown that laboratory assessment of rotproofing should be carried out by more than one method: a treatment which confers a measure of resistance to microorganisms under one set of test conditions may be much less effective when tested by a different procedure. This confirms the findings of many other workers.

AUTHORS

Development of Crease-resist Finishing as illustrated by Patent Rights. F. Duhm. *Melliand Textilber.*, **36**, 938–940 (Sept. 1955).

A brief review of the German position with special reference to drying methods. S. R. C.

Control of Appearance Changes due to Soiling—Mechanism, Measurement, and Reduction of Soiling Changes in Carpets during Use. P. A. Florio and E. P. Mesereau. *Text. Research J.*, **25**, 641–649 (July 1955).

A method is described for the controlled deposition of soil and for the measurement of soil retention by carpets. The mechanism of soil deposition and retention and the reduction of soiling are described. Practical methods for the maintenance of the colour and the texture of carpets by the reduction of soiling are described. By using a soil-retarding finishing treatment consisting of a combination of oxides, preferably alumina and silica having a particle size distribution of 0·1–4·0 μ., it is possible to maintain the original appearance of the carpet for periods three to four times as long as usual. Further improvement in the effectiveness of the treatment may be obtained by the use of oil-free backing yarns and fibres of round cross-section. The treatment is believed to operate by saturation of the sites normally occupied by soil with particles of oxides. Used in concentrations of 0·75–1·0% of dry solids based on the weight of the pile showing, it has been found to be satisfactory for all carpet fibres including wool, viscose rayon, cellulose acetate, nylon, jute, and cotton. The oxides are applied as a dispersion, by spraying before the final drying operation. The finish is removed by three or four professional cleanings after the first shampooing; but re-application can be made by rotary brush or tank sprayer. W. P. M.

Use of Silicones in the Textile Industry. T. W. Watson. J.S.D.C., **71**, 641–644 (Nov. 1955).

The history and the manufacture of silicones are outlined. Silicone products are already being used to confer water-repellency on textile fabrics. They are easily applied and are compatible with many other finishing agents, the water-repellency being achieved by a heat cure of the treated material. In addition, other silicones of value to textile finishers are discussed, and the advantages of certain silicone products for textile machinery maintenance pointed out. AUTHOR

Inflammability of Materials and its Measurement. M. L. Amy. *Chim. et Ind.*, **74**, 526–536 (Sept. 1955).

The importance of the fireproofing of materials to the Paris police department has prompted the investigation described in this paper, which deals with theoretical and practical aspects of flame formation, the inflammability of textile materials, wood, and plastics, and the causes of fires in public buildings. B. K.

PATENTS

Decatising or Steam Setting of Thermoplastic Textiles. C. R. Holroyd. *BP* 735,947

The batched fabric is placed in the machine which is then filled with steam so as to preheat the machine, particularly the perforated roller, and then steam is blown through the fabric from within the perforated roller. This avoids danger of condensate forming within the roller. C. O. C.

Heat Setting of Nylon Fabrics. Triangle Finishing Corpn. *BP* 737,311

Knitted nylon fabric while stretched laterally has hot air blown transversely upon its upper face. The hot air is caused to pass through the fabric and is withdrawn from below it. This treatment is such that the fabric is brought to 150–500°F. for 2–30 sec., the temperature and time being so selected that the fibres neither melt nor become yellowed. Finally the fabric is cooled while still stretched, e.g. by spraying with water. C. O. C.

Setting Thermoplastic Fabrics. E. B. Bates. *BP* 734,488

The dry material is pressed against a moving metal surface, e.g. a drum, by means of an endless belt or the like. The temperature of the metal surface is 120–250°C. and the material is in contact with it for 10–15 sec. C. O. C.

Acetylating Cellulose. S. *BP* 736,618

Cellulose is acetylated without loss of fibrous structure by adding to the acetylating mixture an acid amide soluble therein and as catalyst a product obtained by treating an acetylating agent with sulphuric acid, a derivative thereof containing a sulphuryl radical or a salt thereof. A sample of the liquor which has been boiled after addition of water or dilute mineral acid should not show a total acid concentration > 2 N. C. O. C.

Acylating Hydroxylic Cellulose Derivatives. Hercules Powder Co. *BP* 737,919

Cellulosic materials containing hydroxyl groups, e.g. hydroxyethyl cellulose, are readily acylated by use as catalyst of an equilibrium mixture of (1) perchloric acid and a metallic chloride, bromide, phosphate or sulphonate or (2) a metallic perchlorate and hydrochloric, hydrobromic, phosphoric or a sulphonic acid. The metal of the salt has an electrode potential of 1·7 to −0·7 v. C. O. C.

Wrinkled Textile Fabric. Cranston Print Works Co. *USP* 2,695,653

Unidirectional wrinkles are produced by pressing the moistened fabric in various directions perpendicular to its length and then preferably passing the wrinkled fabric through a high pressure mangle and then can drying it. If a resinous fixing material is present in the fabric then the wrinkled finish resists repeated washings. C. O. C.

Combined Flame-resistant and Water-repellent Finish for Cellulose. Courtaulds. *BP* 736,598

The material is impregnated with an aqueous paraffin wax emulsion containing 8–12% by wt. of ammonium sulphamate. The dried material should show an increase in weight of 9–12%. C. O. C.

Polysiloxane Water-repellent Finishes. Société des Usines Chimiques Rhône-Poulenc. *BP* 736,184

Textiles are impregnated with a mixture of 15–60% by wt. of a methyl polysiloxane resin of CH_3:Si ratio 1·3–1·7, and 15–45% of a methyl polysiloxane oil of CH_3:Si ratio of 1·9–2·1 and 15–65% of butyl titanate, in an organic solvent. On drying a water-repellent finish is obtained which has good resistance to washing. C. O. C.

Finishing Polyamide Materials with Acids or Peroxides. Radiner & Co. *BP* 734,493

Inorganic or organic acids or hydrogen peroxide can be used to modify the properties of polyamide materials in many ways, e.g. to improve the affinity for dyes, reduce lustre, permanent embossing, etc., depending upon the conditions of treatment. Thus better affinity for dyes and differential shrinkage in fabrics containing different polyamide fibres are obtained by treatment for 5–60 sec. and at $>$ 100°C. with either 10–60% by wt. or an organic acid, 2–50% of an inorganic acid or 5–40% of hydrogen

peroxide so as to produce a superficial action on the fibres without appreciable injury to the mechanical properties of the material. C. O. C.

Pile Fabric. Palladium. *BP* 736,355

One face of a textile fabric is coated with a synthetic rubber composition, this coating being permeable to air but not to water. This coating is dried and a second coating of either synthetic or natural rubber applied to it. Pile fabrics are then applied perpendicular to it by means of an electrostatic field produced by very high voltage and finally the rubber coatings are vulcanised. C. O. C.

Pile Material. BrC. *BP* 738,290

The pile is formed on an adhesive-coated fabric by projecting the pile fibres into it by any suitable means. The adhesive consists of a linear condensation polymer which because of suitably spaced NH groups in its main chain can be cross linked to yield a rubbery polymer and a cross linking agent. After application of the pile the whole is heated to cause cross-linking. Thus a suitable adhesive for a fabric where cellulose acetate is in the backing and/or pile consists of a solution, in methylethylketone diluent with a volatile non-solvent for cellulose acetate, of a 1:6-hexamethylene diisocyanate-modified condensation polymer of 5:6:1 mol. of ethylene glycol, adipic acid and monoethanolamine, together with 2:4-dichloronaphthol and the hexamethyl ethers of hexamethylolmelamine. C. O. C.

Mixed Fabrics for use as Interlinings in Fused Fabric Assemblies. Trubenised (Gt. Britain). *BP* 736,851

When using the process described in *BP* 587,162 (*J.S.D.C.*, **63**, 310 (1947)) use of a plasticiser having melting point 40–100°C., e.g. a mixture of acetanilide (50%), formanilide (27·5%) and formo-*o*-toluidide (22·5%) or of acetanilide (90%) and benzyl benzoate (10%), prevents the plasticised materials becoming clammy at ordinary temperatures with consequent difficulties in sewing the assembly before fusion. C. O. C.

Applying a Permanent Dressing to Fabric Articles. Bradford Dyers' Assocn. *BP* 734,587

The dressing agent, e.g. a resinous precondensate, is applied to the article and then curing or setting of the agent is at least initiated and the article compressively shrunk in one operation. C. O. C.

Felted Fibrous Non-woven Porous Fabrics—Leather Substitute. DuP. *BP* 737,137

A leather substitute consists of a non-woven fibrous sheet bound with a soft elastomeric polymer, the ratio of fibres to polymer being from 1:2 to 2:1. The fibres constitute 40–70% of the volume of the finished product. C. O. C.

Felt-base Floor Covering. Armstrong Cork Co. *USP* 2,696,447

A saturated felt backing is coated first with a paint; and then with a vinyl resin coating. The paint is made up of (1) 80–50% of an inert filler and (2) 20–50% of a mixture of 20–60% of a resin compound and 80–40% of a mixture of a vinyl resin and a rubber-like polymer. These give excellent adhesion of the top vinyl coating and the whole is resistant to alkali. C. O. C.

Reducing the Felting Power of Wool. Montclair Research Corpn. and Ellis Foster Co. *USP* 2,696,448

The wool is treated with water soluble derivatives of nylon. C. O. C.

Decatising. Sellers & Co. (Huddersfield). *BP* 738,028

If air at 60 lb. pressure is passed through the cloth immediately after the steam and in the same direction, then the steaming time may be reduced by 20% and the cooling time by 33%, cooling being done by air being drawn through the cloth in the usual manner. C. O. C.

Reducing the Tendency of Textiles to Absorb and Retain Dirt. Boehme Fettchemie. *BP* 738,379

The materials are impregnated with an aqueous solution containing 0·5–10·0 g. per litre of a water-soluble derivative of a polyalkylene oxide wax containing at least one aliphatic, *cyclo*aliphatic or aromatic-*cyclo*aliphatic radical linked through O, S or N, preferably through an ester or amide group to the polyalkylene oxide wax radical. The wax should have mol. wt. > 199, e.g. monostearic acid polyethylene glycol ester. C. O. C.

Yarn Setting (I p. 738).
Embossing (I p. 739).
Textured Pile Fabrics (VI p. 750).
Dry-cleaning and Weatherproofing Fabrics (VII p. 751).
Dyeing and Finishing of Cellulose Triacetate Yarns and Fabrics (VIII p. 751).
Flock Prints and Panne Effects (IX p. 754).
Identification of Insect Damage on Wool and Related Animal Fibres (XIV p. 758).
Flammability of Fabrics (XIV p. 759).
Achievement of High Wear-performance in Rayon Staple Fabrics with Crease-resistant Finishes (XIV p. 759).
Factors influencing Emulsion Stability and Viscosity (XV p. 760).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Some Problems in the Chemistry of the Hemicelluloses. E. L. Hirst. *J.C.S.*, 2974–2984 (Aug. 1955).

This is the fourteenth Pedler Lecture and its main theme is the molecular structure of the so-called hemicelluloses. These are the non-cellulosic materials which are extracted by aq. alkali from the cell walls of liquefied material after the liquid has been rendered water-sol. by treatment with chlorine or sodium chlorite. In general, the hemicellulose fraction contains a number of different polysaccharides, and several kinds of sugar residues are concerned in their mol. structure, notably D-xylose, L-arabinose, D-galactose, L-rhamnose, D-mannose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, and possibly D-galacturonic acid. Their function is probably to give strength and rigidity to the cell walls. The problem of the order in which these residues are arranged becomes formally very similar to that of assigning a detailed mol. structure to a protein. Modern research methods such as hydrolysis with acid followed by qual. and quant. chromatographic analysis, the action of periodate ions, enzymic degradation, X-ray analysis, viscosity determinations, and light-scattering and osmotic-pressure measurements are discussed at length. Structures are represented for esparto xylan, xylose oligosaccharides from maize-cob xylan, wheat-flour xylan, arabo-xylan from esparto, the xylans of pear cell-wall, beech-wood, and algae, β-glucosan from barley, and guaran. H. H. H.

PATENTS

Acidic Organic Mercurial Composition for Rot-proofing Papermaking Stock. F. W. Berk & Co. Inc. *BP* 736,387

Papermaking stock may be treated with a solution of a mercurial composition containing a mercury compound of the general formula Y Hg X (Y = Ar; X = acetate, hydroxide, borate, or lactate) as solute, e.g. phenyl mercuric acetate and acetic acid and lactic acid as solvent, the proportions of the acids being 80–20% to 20–80%. S. V. S.

Sizing of Paper. British Bewoid Co. *BP* 736,803

In making high wet strength paper the stock is sized with a mixture of a mechanically dispersed rosin emulsion containing a protective colloid, e.g. casein, and an inert filler, e.g. finely-divided kaolin, and as a wet strength agent, a urea-formaldehyde syrup, whereby the latter becomes effective on drying the sized paper stock. S. V. S.

Coated Paper. Paper Patents Co. *BP* 737,433

Rotogravure printing paper is made by applying to one or both surfaces of a base sheet a mineral coating material containing a pigment and an adhesive comprising a latex emulsion of latex and a carbohydrate, practically all the latex particles ranging from 0·2 to 0·5 microns in size, and disposing the latex particles chiefly at the surface of the sheet by breaking the emulsion. The base sheet may be formed from pulp having a relatively loose fibre to fibre bond at pH 4–7, and the coating material has pH 7·0–10·5. A fatty acid anti-dusting agent and a latex stabilising agent may be incorporated in the coating. S. V. S.

Metal-filled Carbon Paper and Hectographic Paper. Aktiengesellschaft für Papier und Bürobedarf. *BP* 736,745

Carbon and copying papers of all kinds are produced from base papers containing as filler a finely-divided metal, e.g. aluminium or bronze powder, and having a colourless compensating coating of wax, natural resin, synthetic resin, shellac, chlorinated rubber or similar substances. S. V. S.

Felted Cellulose Acetate Fibres. S. *BP* 737,920

Cellulose fibres are acetylated to not higher than the diacetate so as to retain their fibrous structure and are then made into sheets, or the like. S. V. S.

Stabilising Ethylcellulose. Hercules Powder Co. *BP* 736,303

The colour and viscosity of ethyl cellulose are stabilised by extracting with an acidified aqueous swelling medium, e.g. *iso*propanol and hydrochloric acid, at pH 1·5–3·5, washing out the excess acid, and adding 0·5–1% of a phenol, e.g. di-*tert.*-amylphenol, to the last washing liquor. W. G. C.

Improving the Thermal Stability of Cellulose Esters. Hercules Powder Co. *BP* 736,964

Discoloration by heat of cellulose acetate prepared in the presence of sulphuric acid catalyst, is reduced by treating an aqueous slurry with a water soluble inorganic chlorite, e.g. sodium chlorite at < pH 7 in the presence of acetic acid, phosphoric acid or an acid phosphate. W. G. C.

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Comparison of Different Methods for Dressing Fur Skins. F. Stather, H. Herfeld, and S. Beyer. *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.* (II) 60–78 (1955): *Chem. Abs.*, **49**, 11307 (25 Aug. 1955).

Semi works scale tests with rabbit skins confirmed that the Leipzig pickle alone does not yield a sufficiently water-soluble product, irrespective of whether or not the skins are neutralised. Tanning with HCHO or Cr gave good results under suitable conditions. Combined HCHO–Al tannage showed no advantage over HCHO alone. Better results were obtained by HCHO treatment before the pickle, even though the HCHO was displaced by the acid in the pickle. For HCHO tannage, the HCHO is added to the pickled skins which are later brought to pH 7·5–8·0. For Cr tannage the pickled skins are brought to pH 3, tanned with 33% basic Cr liquor containing 1·2% Cr_2O_3 on the weight of the centrifuged skins and neutralised with Na_2CO_3 to 50% calculated basicity. The HCHO tanned skins contained about 0·25% HCHO and shrank at 73°c. The Cr-tanned skins contained about 0·7% Cr_2O_3 and shrank at 77–80°c. These are satisfactory shrinkage temperatures for furs. Neither tannage affected dyeing, but the catalytic action of Cr precludes H_2O_2 bleaching. C. O. C.

Surface Chemistry of Synthetic Protein Analogues. VI—Interaction of Urea and Salt with Non-electrolytic Polypeptides. T. Isomura, K. Hamaguchi, and H. Kawasato. *Bull. Chem. Soc. Japan*, **28**, 185–189 (April 1955).

The interaction of urea and salt with four non-electrolytic polypeptides has been investigated from their surface pressure–area relationships. It was found in all cases that the co-area of the molecule was increased with increasing urea concentration in the substrate, whereas the molecular weight was not increased. Salt had little effect. From these results it was concluded that urea entered the surface film, forming hydrogen bonds between adjacent polypeptide chains, and these bonds were fairly strong. It is suggested that, in view of these experiments, the denaturation of proteins by urea may be due to the replacement of hydrogen bonding by urea, thereby allowing the protein chain to open out, with consequent breaking of salt links. The theory that the thiol groups play a special part in urea denaturation may therefore be incorrect. W. J. M.

Ultrasonic Tanning and Dyeing (VIII p. 752).

XIII—RUBBER; RESINS; PLASTICS

PATENTS

Manufacture of Elastomeric Vinyl Resin Films. Union Carbide & Carbon Corpn. *BP* 735,767

The tensile and tear strength of films of plasticised vinyl chloride copolymers are improved by stretching the film at or near its calendering temperature and then cooling rapidly without further tension. W. G. C.

Plasticised Urea–Formaldehyde Resins. N. V. Philips Gloeilampenfabrieken. *BP* 735,796

Aq. solutions of plasticised carbamide resin precondensates are obtained by adding a plasticiser, e.g. tricresyl phosphate, to a viscous aqueous solution of a urea-formaldehyde precondensate which contains 2–6% of aniline on the weight of resin solids. W. G. C.

Floor or Wall Covering. Bird & Son. *USP* 2,696,452

A transparent vinyl film is cast onto a carrier sheet from an organosol, heat cured and a design printed on it. The paint is then coated with a pigmented vinyl organosol, this coating heat cured and the whole bonded to asphalt saturated felt and finally the carrier stripped off. C. O. C.

Improving the Printing Properties of Polyethylene (IX p. 754).

Felted Fibrous Non-woven Porous Fabrics—Leather Substitute (X p. 756).

XIV—ANALYSIS; TESTING; APPARATUS

Surface Thermometer for measuring the Surface Temperature of Drying Cylinders. A. T. Carlander and L. Jordanason. *Svensk Papperstidning*, **58**, 616–620 (15 Sept. 1955).

A surface thermometer for continuous use on drying cylinders consists of a resistance unit located in front of a concave metal reflector and placed about 1 mm. from the cylinder surface. A six-point chopper bar recorder registers the temperature. The results correlate well with those obtained from a similar element fixed to the cylinder surface. S. V. S.

Electrostatic Charge Detector and Measuring Device. G. Maggi. *Securitas* 3 (Italy), **39**, 84–7 (May–June 1954): *EPA Technical Digest* No. 30.

New Objective Glossmeter. L. F. Hopkins and A. P. Highton. *Proc. Tech. Sectn. British Paper & Board Makers' Assocn.*, **36**, 339–358 (May 1955).

In an instrument for indicating surface finish by determining the degree of polarisation of a reflected beam of light, the light reflected from the sample passes through a rotating segmented polarising drum, made of sheet polarising material, and through an adjustable analyser of the same material, into a photoelectric cell. Using the latter to detect a null point makes the method independent of the operator and many other variables. S. V. S.

Isolation and Characterisation of Succinic and Glutaric Acids as *p*-Phenylazoanils. H. B. Henbest and T. C. Owen. *J.C.S.*, 2968–2969 (Aug. 1955).

Acids of the succinic and glutaric acid type formed during the oxidative degradation of organic compounds are often isolable only with difficulty. This has now been overcome by conversion of the acids into coloured highly crystalline *p*-phenylazoanils, which are stable to alumina, give deep yellow bands on a chromatogram, and so are readily separated. The acids, after conversion to the anhydrides with acetic anhydride, are treated with *p*-aminoazobenzene in chloroform solution, and the relatively insoluble anilic acids which result (90% yields) are cyclised by means of acetyl chloride in the same solvent to afford the azoanil. H. H. H.

***p*-Phenylazomaleinanil: A Reagent for Conjugated Dienes.** P. Nayler and M. C. Whiting. *J.C.S.*, 2970–2971 (Aug. 1955).

Maleic anhydride when added in chloroform to a soln. of *p*-aminoazobenzene in chloroform gives the anilic acid, and this when stirred at 80°c. with acetic anhydride affords *p*-phenylazomaleinanil. This cpd. is particularly

useful in that it undergoes Diels–Alder reactions with conjugated dienes to form coloured adducts which can be isolated by chromatography on alumina with particular ease because of their strong colour. The adducts are of high m.p. and crystallise well, while the large weight factor is an additional advantage. H. H. H.

Identification of Azoic Diazo Components by Micro-sublimation Tests. W. Kunze. *Textil Praxis*, **10**, 684–686 (July 1955).

Thirty photomicrographs are shown which illustrate the crystals formed by different Fast Bases on sublimation, from which it is readily seen that bases can be differentiated by their crystalline structure. B. K.

Analysis of Coal-tar Colours. K. A. Freeman. *J. Assoc. Offic. Agr. Chemists*, **38**, 353–7 (1955): *Chem. Abs.*, **49**, 10130 (10 Aug. 1955).

Transference of the colours in foods, drugs and cosmetics onto wool and their identification by colour changes produced on the dyed fibres by acid and alkalis are unreliable. Many coal-tar colours decompose during dyeing and stripping and the products may change the hue of the spot test. Mixtures can seldom be completely separated, resulting in misleading results in the spot tests. Presence of non-dye components of the original sample and differences in concentration of the dye on the wool alter the appearance of the spot test. Consequently it is recommended that these methods be deleted from the 8th ed. of *Official Methods of Analysis, A.O.A.C.* Single colours should be identified by comparing their spectrophotometric characteristics with those of known colours, in $CHCl_3$ for oil-soluble colours and in 0·1 N-HCl, 0·1 N-NaOH and dil. aq. NH_4OOCCH_3 for water-soluble colours. Mixtures of water-soluble colours are separated on a column of cellulose powder by adsorption from 20% brine and elution by the same solution so long as any colour moves down the column. If the colour does not move, successively reduce to the NaCl concentration by one half until it does. If two or more bands separate, collect each separately, reducing the NaCl concentration if necessary. C. O. C.

Estimation of Fluorescent Brightening Agents. G. G. Taylor. J.S.D.C., **71**, 697–704 (Dec. 1955).

The paper is limited to comparative strength determination of chemically identical samples. The problems are closely analogous to those of the strength determination of dyes, the differences arising mainly from the nature of the light the source and the small amount of fluorescent light available. Particular difficulties such as the *cis–trans* isomerism of stilbene derivatives are more prominent with fluorescent brightening agents than with dyes. Strength determination in solution is necessarily limited to instrumental methods. The Spekker fluorimeter (Hilger) is discussed in detail, and the method of converting the readings to a function analogous to optical density is given. For strength determination on a substrate, both visual and instrumental methods are discussed. The accuracy of visual estimation is comparatively low, but may be considerably improved by a technique analogous to "cross-dyeing" in dye estimation. No commercial instruments for measurement on substrates exist, but a simple adaptation of the Spekker fluorimeter is described which gives useful results within its limitations. Author

Subsidiary Dyes in D&C Colours. 4-Tolueneazo-2-naphthol in D&C Red No. 35. L. Koch. *J. Assoc. Offic. Agr. Chemists*, **38**, 357–9 (1955): *Chem. Abs.*, **49**, 10130 (10 Aug. 1955).

In a collaborative study of two proposed methods the spectrophotometric procedure (*Chem. Abs.*, **48**, 11791 (1954): J.S.D.C., **71**, 70 (Jan. 1955)) presented least difficulty and gave accurate enough results. Some of the participants obtained erratic results using the chemical procedure (*Chem. Abs.*, **48**, 9695 (1954): J.S.D.C., **70**, 596 1954)). C. O. C.

Methods of Differentiation of Polyamide and other Synthetic Fibres. H. M. Ulrich. *Textil Praxis*, **10**, 747–751 (Aug. 1955).

A summary of physical and chemical tests for the identification of synthetic fibres. B. K.

Selection of Scales for Assessing the Stability to Light of Fibres. A. Sippel. *Textil Praxis*, **10**, 679–684 (July 1955).

Comparison of two methods of assessing the stability to light of textile fibres, viz. tensile strength tests against a standard fibre and exposure against blue standards till a fixed fade is shown. B. K.

Assessment of the Weathering Fastness of Dyed Textiles. E. Butterworth and J. C. Guthrie. J.S.D.C., **71**, 587–592 (Oct. 1955).

Dyed textiles are, in general, less resistant to colour change when weathered than when exposed behind glass to daylight. No standard method exists for the assessment of weathering fastness. An outdoor weathering test and a wet fading lamp test are described, and their merits and deficiencies discussed. The method of assessment allows direct comparison between the weathering (or wet-fading-lamp) fastness of a pattern and the light fastness according to *B.S.* 1006. These methods have yielded useful results in practice, and this paper records some work carried out to date. Authors

Some Textile-destroying Fungi in Israel. *Palestine J. Botany, Jerusalem*, Ser 6, 107–113 (1953): *Chem. Abs.*, **49**, 12011 (10 Sept. 1955).

Penicillium spp., *Trichoderma lignorum*, *Stamphylium verruculosum*, *Alternaria tenuis*, *Stachybotrys atra*, *Memnoniella echinata*, *Chaetomium spirale*, *C. murorum*, *C. pannosum* and *C. erectum* have all been found on infected textiles. The first four caused the most severe damage. Trials with all these species on cellulose textiles are described. C. O. C.

Identification of Insect Damage on Wool and Related Animal Fibres. D. J. Ott. *Amer. Dyestuff Rep.*, **44**, 515–520 (1 Aug. 1955).

A description is given, with 5 photomicrographs, of methods for examining fibres to determine whether they have been attacked by moths or beetles. Examples are given of instances where confusion with burn or mechanical damage is possible, and emphasis is laid on the fact that damage to Mitin-treated fabric can occur from incidental feeders which do not digest the wool they eat and therefore remain alive. J. W. B.

Differential Dyeing as an Indicator of Bilateral Structure in Wool. J. H. Dusenbury and A. B. Coe. *Text. Research J.*, **25**, 354–358 (April 1955).

Adjacent cross-sections of fibres were dyed with basic and acid dyes at various temperatures and pH values. The experiments confirmed the observations of Ohara, of Horio and Kondo, and of Mercer, that the convex outer portion of the crimp curvature of the wool fibre, which is the orthocortex, is preferentially dyed by basic dyes. Contrary to the results of Horio and Kondo and of Ohara, the experiments show that acid dyes, where they exhibit bilateral dyeing behaviour, also dye the convex outer portion of the crimp curvature preferentially. These results were confirmed by those of further experiments. In only one case was the inner portion dyed preferentially by acid dyes. This occurred when Ponceau 2R was dyed on the wool at the boil at pH 7 (Ponceau 2R was used by Horio and Kondo at 60°C.). It was observed that, at the boil, in the phosphate buffer solution used to give a pH of 7, the crimp frequency was drastically reduced regardless of the dye employed. By dissolving (in 10% caustic soda) the orthocortex from fibres dyed with Formyl Violet S4B (outer portion of crimp preferentially dyed) and from fibres dyed at 100°C. with Ponceau 2R (inner portion preferentially dyed), it was shown that, in both cases, the more heavily dyed portion was dissolved. This indicates that the orthocortex is always dyed preferentially and that the crimp is reversed in boiling solutions of phosphate buffers, and it suggests that the phenomenon is associated with the greater reactivity of the orthocortex rather than with differences in the number of dyeing sites in the two portions of the cortex. Further, the results seem to support Harris's criticism of the amino acid analyses of Golden *et al.* (J.S.D.C., **71**, 683 (Nov. 1955)), viz. that abnormally high dibasic amino acid and abnormally small dicarboxylic contents of the paracortex were due to preferential extraction of certain acids from the paracortex by the enzymatic preparation procedure. Also, in recent studies

of β-ACTH it was found that acidic amino acid components were preferentially extracted when an enzyme was used. Thus the assumption of Golden that the orthocortex was extracted cleanly from the paracortex plus epicuticle fraction may be incorrect. W. P. M.

Detergency Measurement using Artificially Soiled Cloths. F. L. Diehl and J. B. Crowe. *Amer. Dyestuff Rep.*, **44**, 677–680 (26 Sept. 1955). See J.S.D.C., **71**, 275 (May 1955).

Flammability of Fabrics. D. I. Lawson, C. T. Webster, and M. J. Gregsten. *J. Textile Inst.*, **46**, T 453–T 463 (July 1955).

A vertical flame-speed apparatus and a semicircular instrument more suitable for general use are described. The first comprises a torsion balance from the arm of which is suspended a 6-ft. vertical strip of material; when this burns the weight-loss causes a swing of the balance arm, which is recorded by means of a parallel beam of light reflected from a mirror on the torsion wire and focussed on a piece of photographic paper wrapped round a slowly rotating drum. Thus the rate of burning is expressed in the form of a graph when the paper is developed. In the semicircular test a strip of fabric 1½ in. × 21 in. is held in a semicircular frame, and the time taken for flame to pass completely or partly round it is measured. Results obtained by both methods on a number of fabrics, including some treated with $NH_4H_2PO_4$, are compared and discussed. For fabrics which burn only partly on the semicircle the vertical flame speed is proportional to the square root of the semicircular distance of burning; for materials burning round the semicircle the vertical flame speed is inversely proportional to the time of burning. With a wide variety of cellulosic materials the vertical speed of burning is inversely proportional to the weight per unit area of the materials. J. W. B.

Achievement of High Wear-performance in Rayon Staple Fabrics with Crease-resist Finishes. H. W. Best-Gordon and T. H. Morton. J.S.D.C., **71**, 874–883 (Dec. 1955).

Details are given of practical wear-assessment of crease-resist-finished rayon staple fabrics with the new Bocking Testing Machine (BFT Mark III). The machine determines resistance to flexing and to ball penetration; from these a duty factor is derived which correlates very well with resistance to premature wear.

Details are given also of the preferential resin pick-up of one fibre over another in blend fabrics, and the duty factors of an *ad hoc* series of satisfactorily produced gabardines.

The effects are described of some substances added to urea–formaldehyde resins for the purpose of producing various finishes on all-viscose rayon staple gabardines, and their effects on the duty factor are also discussed.

Finally, various conditions in the resin treatment of long-staple rayon fabric and their effects on wear-performance assessed by the duty factor are considered in detail. AUTHORS

Microdetermination of Chloride by the Diffusion Technique, and the Chloride Content of Raw Cotton. H. Naylor. *J. Textile Inst.*, **46**, T 576–T 583 (Sept. 1955).

Using a closed diffusion unit, chloride-containing residues obtained from ashed carbonate-impregnated cotton are estimated by oxidising with $KMnO_4$–H_2SO_4 and absorbing the chlorine in sodium arsenite solution. This eliminates the error due to volatilisation of iodine when KI solution is used as absorbent. The chloride contents of 23 different cottons are thus determined. J. W. B.

Quantitative Chemical Analysis of Intimate Mixtures of Secondary Cellulose Acetate with Certain Other Fibres. Tentative Textile Standard No. 33, 1955. *J. Textile Inst.*, **46**, s 101–s 103 (Sept. 1955).

Secondary cellulose acetate is removed from blends with cotton, wool, nylon, Terylene, or viscose rayon by dissolving it in acetone. The mixture (0·5 g.) is weighed (a further 0·5 g. being weighed for moisture determination) and transferred to a stoppered 50-ml. conical flask, where it is shaken with 20 ml. of acetone at room temp. and left for 30 min. The liquid is decanted through a sintered glass filter crucible (preferably with ground glass stopper) and the treatment repeated twice, using 15-min. periods. The residue is washed on to the filter with more acetone, washed with water, dried for 3 hr. at 110°C., cooled, and weighed. J. W. B.

Quantitative Separation of Wool and Man-made Cellulosic Fibres. M. Kehren. *Z. ges. Textilind.*, **57**, 1226–1334 (5 Oct. 1955).

Experimental evidence is provided to demonstrate the superiority of caustic potash (0·3 N. at the boil) over sulphuric acid for quantitative separation of wool and cellulosic fibres in mixtures. B. K.

Instrument for Rapid Estimation of Cross-sections of Single Wool Fibres. G. E. Settle. *J. Textile Inst.*, **46**, T 633–T 640 (Oct. 1955).

A single wool fibre is suspended under constant tension of 1·6 g. (sufficient to unerimp but insufficient appreciably to extend) diagonally across but in the same plane as a slot 100 μ. wide and formed between two parallel glass rods held in brass jaws. Conditioned air is drawn through the slot, and the relation is studied between fibre diameter and the rate of air flow under constant pressure difference. Work leading to the selection of optimum fibre position and tension is described, and it is shown how the fibre diameter can be measured rapidly and easily. At the 5% probability level it is concluded that the diameter of a wool fibre can be assessed with a maximum error of about 1·3 μ.; for smooth fibres like nylon the instrument is as accurate as a microscope. It is of particular value when operated in conjunction with the Instron Tester for determining breaking loads. J. W. B.

Relative Humidity Correction to the Results for Determinations of the Diameter of Wool Fibres by the Air-flow Method. S. L. Anderson. *J. Textile Inst.*, **46**, T 675–T 676 (Oct. 1955).

A table of data is given whereby results of fibre diameter determinations by the air-flow method at humidities other than 65% R.H. can be converted to correspond to 65% R.H. The main effect of humidity on results is considered to be that due to swelling. J. W. B.

Paper Chromatography of Wool–Polyamide Fibre Blends. H. H. Bühler and H. Zahn. *Melliand Textilber.*, **36**, 980–981 (Oct. 1955).

Separation of the hydrolysates of wool and polyamide fibres by two-dimensional paper chromatography is described. S. R. C.

Identification of the Non-wool Component in Binary Mixtures of Wool and Certain Other Fibres. Tentative Textile Standard No. 34, 1955. *J. Textile Inst.*, **46**, s 104–s 106 (Sept. 1955).

The non-wool component in binary mixtures of wool and staple forms of cotton, silk, viscose rayon, cuprammonium rayon, secondary acetate rayon, cellulose triacetate, regenerated protein fibres, Orlon, Ca alginate, nylon, and Terylene is identified by applying the following scheme. The sample is washed in petroleum ether, dried, and examined under the microscope to confirm the presence of wool + unknown. Eight tests are made and are followed in order, consisting firstly in treatment with acetone, methylene chloride, and boiling $Ba(OH)_2$–KNO_3 mixture. Evaporation of the first two solvents on a watch glass confirms secondary acetate or triacetate. If there is a residue from the $Ba(OH)_2$–KNO_3 treatment it is dried and flame-tested, which permits classification into groups. Further portions of this residue are treated with one of the following, according to the flame test: cold conc. HCl (silk dissolves); cold 59% H_2SO_4 (viscose and cupra-ammonium rayons dissolve in 1 min.; cotton is insoluble); cold 5 N-HCl for 1 min. (6- and 6,6-nylon dissolve; Terylene and Orlon are insoluble); cold conc. HNO_3 (Orlon dissolves within 30 sec.; Terylene is insoluble). J. W. B.

Soil-infection Method for Testing of Textiles for Resistance to Microbiological Attack. A. O. Lloyd. *J. Textile Inst.*, **46**, T 653–T 661 (Oct. 1955).

Ancillary factors involved in assessing the efficiency of rotproofing and mouldproofing treatments are discussed,

and a method is described in which the physical conditions are standardised to a greater degree than previously. Strips of cloth are coated along the central portion, using a Perspex mask, with a 3 in. × 1 in. × $\frac{1}{16}$ in. layer of soil–compost–kieselguhr paste. They are suspended with ends together and centre hanging as a loop in a Perspex container, the paste composition being on the outside of the loop. Inside the lower part of the loop is inserted a preformed asbestos plug 1 in. × $\frac{3}{4}$ in., consisting of 2·5 g. asbestos and 7·5 g. water; this serves to keep the specimen moist. The container is filled to a depth of 1 in. with water; if necessary, more water can be added to the plugs during incubation. Satisfactory use has been obtained over the range 26–32°C., and results are briefly described of experiments using pentachlorophenyl laurate, where good reproducibility is obtained. It is suggested that the pH value of the inoculum should be 6–7·5. J. W. B.

Determination of the Constituents in Asbestos–Glass–Organic Fibres Textile Materials. G. Satlow. *J. Textile Inst.*, **46**, T 631–T 632 (Sept. 1955).

A method of double ignition is available for ternary blends of asbestos, glass, and organic fibres, firstly at 500°C. and then at 900°C. At these temperatures the respective losses are— chrysotile asbestos 2·6% and 14·5%, glass 0·3% and 0·5%, and organic fibres 99% and 99%. Formulae are given for calculating the three percentages from weights of residues obtained at these temperatures. J. W. B.

Measurement of Surface Pigmentation in Animals. A. J. Lea. *Nature*, **176**, 558 (17 Sept. 1955).

A previously reported method (*Ann. Human Genetics*, **19**, 97 (1954)) for determining the pigmentation of human and mammalian hair also gives reproducible results with feathers, amphibian and fish skins, and insect scales. It is probable that it is applicable to the estimation of surface pigmentation in all types of animals. J. W. B.

Two New Methods for Determining the Acidity of Vegetable-tanned Leather. D. Burton and L. Ma. *J. Soc. Leather Trades Chem.*, **39**, 286–300 (Sept. 1955).

The leather, containing <5% moisture, is immersed for 6–8 hr. in pure methanol, and then extracted for 30 hr. in a Soxhlet apparatus with the same solvent. For mineral acidity, the alcoholic extract is reduced by evaporation, diluted with dist. water, boiled for 1–2 min., cooled, and titrated with NaOH (0·1 N.) to pH 4. For org. acidity, the alcoholic extract is concentrated, dil. with dist. water, and dist. to remove the alcohol completely; the cooled aq. soln. is titrated as above, to pH 7. The free strong acidity can also be determined accurately by immersing the dried leather for 48 hr. in a soln. containing anhyd. sodium acetate (5 g.) in 1 litre of a 1 : 1 mixture of pure ethylene glycol and pure *iso*propanol, with periodic shaking. The leather is separated by filtration, and an aliquot of the filtrate is titrated with HCl (0·25 N.) in the above solvent mixture under prescribed conditions. The free mineral acidity is calc. from the decrease in the amount of HCl required, due to its reaction with the sodium acetate. Numerous analyses are cited, and there are two sketches of the apparatus required. J. W. D.

Determination of Silica and Aluminium in Chrome Leather. A. Danon. *Rev. Tech. Ind. Cuir*, **47**, 168–170 (Aug. 1955).

The official method for the determination of Al in chrome leather (*S.L.T.C. Official Methods of Analysis* (1951)) is subject to ten sources of error; these are cited and briefly discussed. The Al contents of a number of leathers have been determined by direct application of the official method, and also with prior removal of the SiO_2 by treatment with HF. It is emphasised that the determination of Al must be preceded by the removal (or determination) of SiO_2, otherwise the two are pptd. together. The determination of SiO_2 should be added, it is recommended, to the official methods for the analysis of leathers. J. W. D.

PATENTS

Wear-testing Machine for Fabrics. U.S. Secretary of the Army. *USP* 2,696,736

A simply constructed machine which subjects the fabric to tension, flexing, compression, shear and rubbing during each cycle. It is so made that each of these factors can be varied in kind and intensity. C. O. C.

Apparatus for Defining the Percentage of Moisture in Electrically Relatively Non-conducting Materials. H. Eicken. *BP* 737,145

A moisture regain apparatus, suitable for textiles, comprises a thermionic valve the grid of which is arranged to have a voltage of one polarity applied to it through a reactance and to have a rectified pulsating voltage of the opposite polarity applied to it through two feelers between which lies the material under test. The feeler remote from the grid in the grid circuit is earthed, and means are provided in the valve anode circuit to give a consequent response in accordance with the moisture content. These means may comprise an electronic system having two thyratrons which are operated by the thermionic valve, one thyratron being operated when the moisture content is a predetermined amount above a reference value and the other when the content is below a reference value. The thyratrons can be arranged to control a machine designed to bring the moisture content within a predetermined range. J. W. B.

Colour-perception Testing Apparatus. British Transport Commission. *BP* 740,365

The light source is provided by illuminated magnesium carbonate. Where several apertures containing colour filters are to be illuminated from a single source the magnesium carbonate reflectors are arranged with their reflecting surfaces lying on a part of the concave surface of a sphere with the originating source of light at the centre of the sphere. This gives equal brightness of illumination from each reflector and so precludes assessment of colour by relative brightness. C. O. C.

Density of Modified Cottons determined with a Gradient Column (VI p. 749).

Control of Appearance Changes due to Soiling— Mechanism, Measurement, and Reduction of Soiling Changes in Carpets during Use (X p. 755).

Inflammability of Materials and its Measurement (X p. 755).

XV— MISCELLANEOUS

Auguste Rosenstiehl (1839–1916). M. Ringeissen. *Teintex*, **20**, 700–703 (Sept. 1955).

A short biography. S. R. C.

Factors influencing Emulsion Stability and Viscosity. P. Sherman. *Research*, **8**, 396–401 (Oct. 1955).

Discussion of the influence on the viscosity and stability of emulsions of such factors as the viscosities of both external and internal phases, nature of the emulsifying agent and particle size distribution. Until closer correlation between theoretical and applied aspects is obtained we are, despite the abundance of general data on the viscosity and stability of emulsions, far from an accurate appreciation of the mechanisms involved. 40 references. C. O. C.

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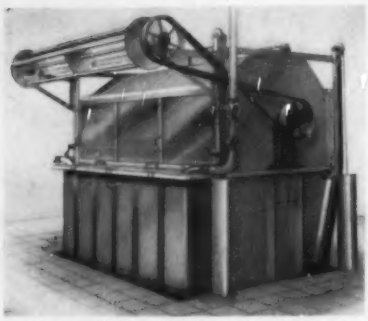
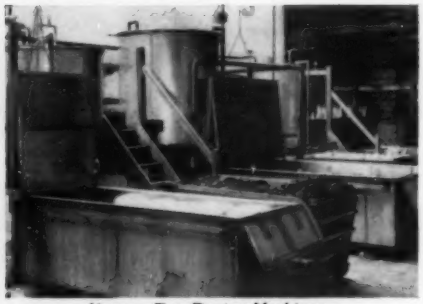


Above — Enclosed Piece Dyeing Machines

Above — Loose Wool Dyeing Plant



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Chapman, E. D., formerly of 221 Slade Lane, Levenshulme, Manchester 19, to 22 Ford Lane, Didsbury, Manchester 20

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Donaldson, R. S., formerly of 4 Cocksheadey Road, Bollington, Macclesfield, to 10 Elmfield Road, Davenport, near Stockport, Cheshire

Duckworth, H., formerly of 461 Blackburn Road, Edgworth, near Bolton, to 14 Geoffrey Avenue, Leek, Staffs.

Dunlop, J. C., formerly of 73 The Promenade, Southport, Lancs., to 22 Weld Road, Birkdale, Southport, Lancs.

Eastwood, P., formerly of 3 Chapel Avenue, Hebden Bridge, Yorks., to "Birchcliffe", 2 Woodland Drive, Princes Park, Shevington, near Wigan

Edwards, H., formerly of 239 Denton Lane, Chadderton, Oldham, to "Newlyn", 10 Carr Lane, Greenfield, near Oldham

Gatenby, F. D., formerly of 37 High Park Crescent, Heaton, Bradford, to 48 Clovelly Street, Rochdale, Lancs.

Harris, Miss P., formerly of 82 Manchester Road, Fairfield, Manchester, to 109 Manchester Road, Fairfield, Manchester

Holdsworth, R., formerly of 1 Rosemary Lane, Raistrick, Brighouse, Yorks., to 25 Harriet Street, Brighouse, Yorks.

Hopkinson, Geo. G., formerly of Wilmer Field, Heaton, Bradford, to Tree Tops, 9 Church Lane, Adel, Leeds 16

Hughes, F. W., formerly of 177 Upper Dale Road, Derby, to 546 Nottingham Road, Chaddesden, Derby

Illingworth, F., formerly of "Eldroth", Greencliffe Avenue, Baildon, to "Stone Croft", West Lane, Baildon, Yorks.

Lascaris, L., formerly of 23 Thorp Avenue, Fieldhouse, Holmfirth, Huddersfield, to Bourse Hotel, Bourse Street, Canta, Egypt

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Mchaffy, P., formerly of 65 Cumberland Road, Dundonald, Belfast, to "Shangarry", Doagh Road, Cloughfern, Whiteabbey, Co. Antrim

2736809, J/T, Marriott, F. W., formerly of Hut X31, No. 2 Wing, 2 R.S., R.A.F. Yatesbury, Calne, Wilts., to Block 3, Room 2, R.A.F. Leuchars, Fife, Scotland

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Midgley, P. G., formerly of 41 Green Terrace Square, Savile Park, Halifax, to 7 Oaklands Avenue, Northowram, Halifax, Yorks.

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Oldfield, N., formerly of 28 Raines Crest, Milnrow, Lancs., to 18 Richmond Road, Coulsdon

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Ramadan, A. S., formerly of 28 St. Pauls Road, Manningham, Bradford, to Beida Dyers, Dyeing Dept. Alexandria, Egypt

Richards, F., formerly of 41 Woodman Drive, Bury, Lancs., to 5 Kendal Avenue, Norden, near Rochdale, Lancs.

Roberts, R. J., formerly of 12 Brightside Road, Leicester, to 11 Chapel Lane, Knighton, Leicester

Roberts, S. K., formerly of I.C.I. Ltd., 4 Blythswood Square, Glasgow, C.2, to 42 Deansgate, Manchester

Satterthwaite, E. M., formerly of 64 Leicester Road, Thurcaston, Leicester, to 8 Northcote Road, Knighton, Leicester

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Crook, B., formerly of 196 Wentworth Street, W., Magog, Quebec

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Gee, B. C., formerly of 2 Cherryhill Drive, Ballyregan Road, Dunronald, Belfast, Northern Ireland

Green, A. N., formerly of 19 Salcombe Road, Basford, Nottingham

Hatton, C. A., formerly of 206 Blackpool Road, Lea, near Preston

Kosprek, A. E., formerly of 15 Huntley Street, Hamilton Street, Ontario, Canada

Kupczyk, J., formerly of 5 Rutland Grove, Farnworth, Lancs.

Levy, J. B., formerly of Lowell Textile Institute, Lowell, Mass., U.S.A.

Meier, P. W., formerly of Oberwilerstrasse 38, Basle, Switzerland

Moore, G., formerly of 20 Welwyn Avenue, Wrose, Shipley

Morrison, A., formerly of America Woollen Co., P.O. Box 930, Lawrence, Mass., U.S.A.

Partington, G., formerly of Textile Department, Ontario Research Foundation, 43 Queens Park, Toronto 5, Ontario, Canada

Stamires, D., formerly of 9 Shaw Lane, Leeds 6

Standring, Dr. P. T., formerly of I.C.I. Ltd., 1200 St. Alexander Street, Montreal, Canada

Stevenson, Mrs M., formerly of 46 Mountside Crescent, Prestwich, near Manchester

Stiassny, K., formerly of 70 Bialik Street, Ramat Gan, Israel

Swift, F. S., formerly of 3 St. Annes Street, Ennis, Co. Clare, Eire

a Viscosa, C. I. S., formerly of Dvozione Centrale degh Etabiliment (Dott. Calandra), Via Sicilia 162, Roma, Italy

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SITUATIONS VACANT AND WANTED *etc*

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed BOX —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

SITUATIONS VACANT

The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

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MISCELLANEOUS

THE SOCIETY has requests for January to June and September 1955 issues of the *Journal*. If any member wishes to dispose of any of these copies, the Society will re-purchase them at 2/– per copy. Replies to be addressed to the General Secretary, Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1.

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FORTHCOMING MEETINGS OF THE SOCIETY

continued from page xiv

Wednesday, 21st March 1956

MIDLANDS SECTION. *Fast Dyes on Cellulose Triacetate.* J. G. Graham, Esq., B.Sc. (Joint Meeting with British Association of Chemists). Midlands Hotel, **Derby.** 7 p.m.

Thursday, 22nd March 1956

MIDLANDS SECTION. *Dyeing Faults in the Carpet and Hosiery Industries.* G. H. Lister, Esq., B.Sc., Ph.D. (Joint Meeting with the Textile Institute). Carpet Trades Canteen, **Kidderminster.** 7 p.m.

WEST RIDING SECTION. Annual General Meeting. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 23rd March 1956

LONDON SECTION. *Dyeing of Narrow Fabrics—Cellulosic and New Fibres.* Dr. I. M. S. Walls (I.C.I. Ltd.). George Hotel, **Luton.** 7 p.m.

Saturday, 24th March 1956

NORTHERN IRELAND SECTION. Annual General Meeting and Dinner. Details later.

Tuesday, 10th April 1956

SCOTTISH SECTION. *Textile Invention and the Dry Cleaner.* A. J. Crockatt, Esq., M.Sc., F.R.I.C. (Eastmans Dyers and Cleaners Ltd.). St. Enoch's Hotel, **Glasgow.** 7p.m.

Saturday, 21st April 1956

BRADFORD JUNIOR BRANCH. Annual General Meeting. Technical College, **Bradford.** 10.15 a.m.

Wednesday, 25th April 1956

HUDDERSFIELD SECTION. Visit to Messrs. Stevensons Dyers Ltd., **Ambergate,** Derbyshire.

MIDLANDS SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. Kings Head Hotel, **Loughborough.** Preceded by the Annual General Meeting of the Section. 6.30 p.m.

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Apperley, T. W. J., Dept. of Colour Chemistry and Dyeing, The University, Leeds 2
Ashruff, A. O. S., Nottingham and District Technical College, Shakespeare Street, Nottingham
Barrett, F. M., "Sunnymeade", 47 Blakelow Road, Macclesfield, Cheshire
le Bek, I. A. G., 8 Lad Hill Lane, Greenfield, near Oldham
Broadley, H., "Kelvin Park", Hurstbridge, Victoria, Australia
Brooke, F. M., 51 Victoria Drive, Horsforth, near Leeds
Carter, A., 4 Alexander Park, Armagh, County Armagh, Northern Ireland
Edge, E. N., 117 Crompton Way, Bolton, Lancs.
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Evans, N. A., 199 Withington Road, Whalley Range, Manchester 16
Grey, J., 11 Wellstead Avenue, Lower Edmonton, London N.9
Hamilton, W. K., 3 Hamilton Place, Neilston, near Glasgow
Henshall, H. E., "Longwall", 12 Cleaver Avenue, Belfast, Northern Ireland
Jackson, C. F., "Wendover", Cavendish Road, Bowden, Altrincham, Cheshire
Jain, S. K., Technical Chemistry Department, Royal Technical College, Glasgow C.1
Jliadis, S., Nottingham and District Technical College, Shakespeare Street, Nottingham
Kanawaty, G. D., 7 Hatassou Street, Sidi Gaber, Alexandria, Egypt
Khachoyan, J., Compagnie Francaise des Matières Colorantes (Francolor), Villers, St. Paul (Oise), France
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Olive, L. W., 44 Heathside Road, Withington, Manchester 20
Patel, N. J., 132 Deramore Avenue, Belfast, Northern Ireland
Ramwell, R. O., 10 Forest Range, Levenshulme, Manchester 19
Renaudin, A., Compagnie Francaise des Matières Colorantes, Villers, St. Paul (Oise), France
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Szolin, J., 2 Alexandra Gardens, Alexandra Street, Nottingham

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Hobson, G. J., 21 Batcliffe Drive, Leeds 6
Lavigne, L. H. D., Provincial Institute of Textiles, 196 Wentworth Street, North, Hamilton, Ontario, Canada
Papadimitriov, D. K., 20 St. Paul's Road, Manningham, Bradford
Plumb, N. J., 5 Mitchell Avenue, Halstead, Essex
Ridsdale, J. B., "Algoa Villa", Wibsey Park Avenue, Bradford 6
Robinson, W. J. R., c/o Hilwee Bleaching Co., Dunmurry, Belfast, Northern Ireland
Smith, Miss J. P., "Cranbourne", St. Andrews Avenue, Morley, Leeds
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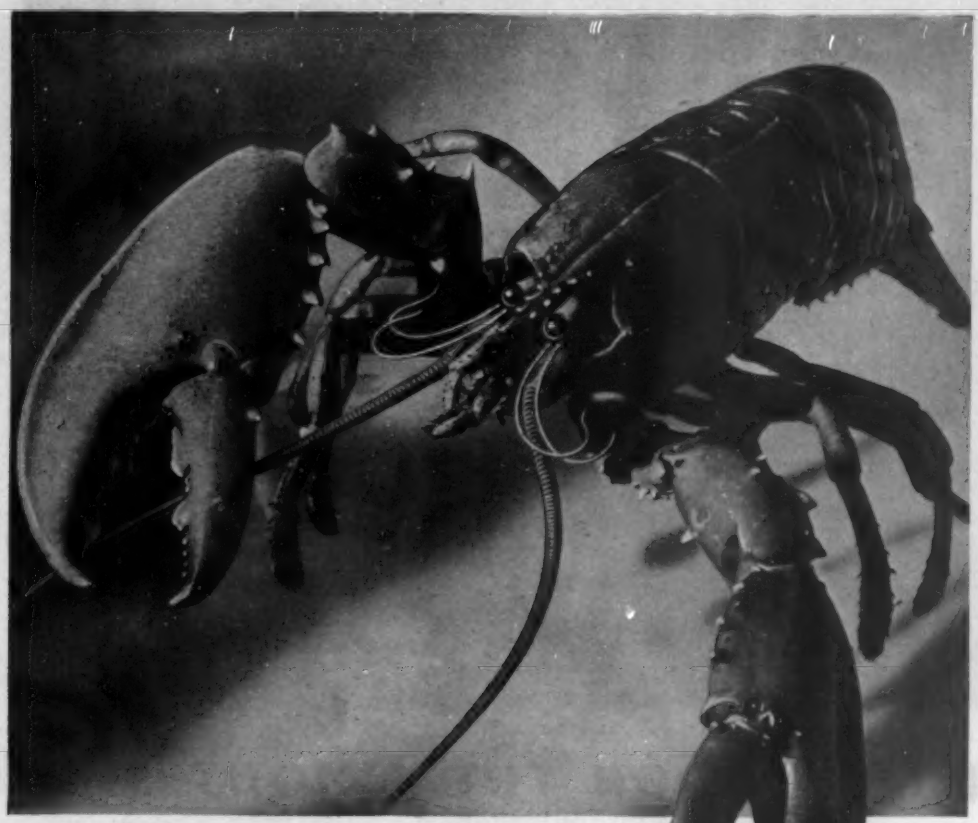

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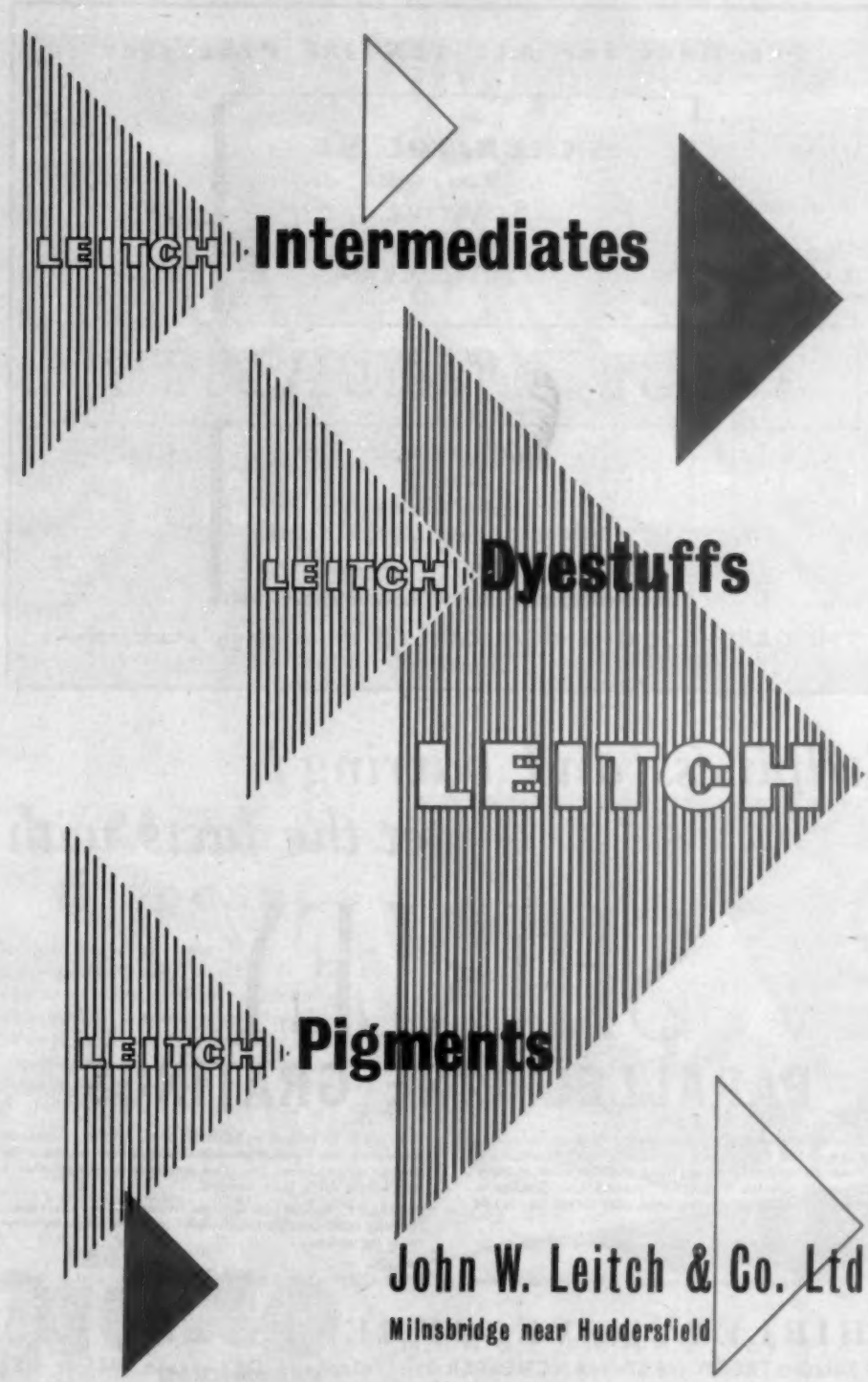
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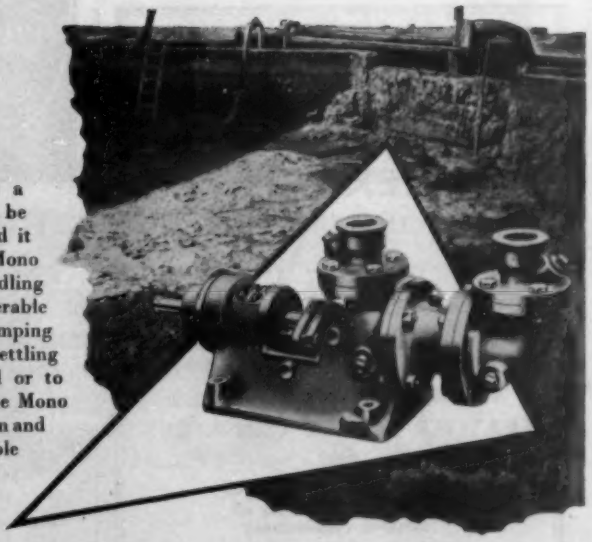

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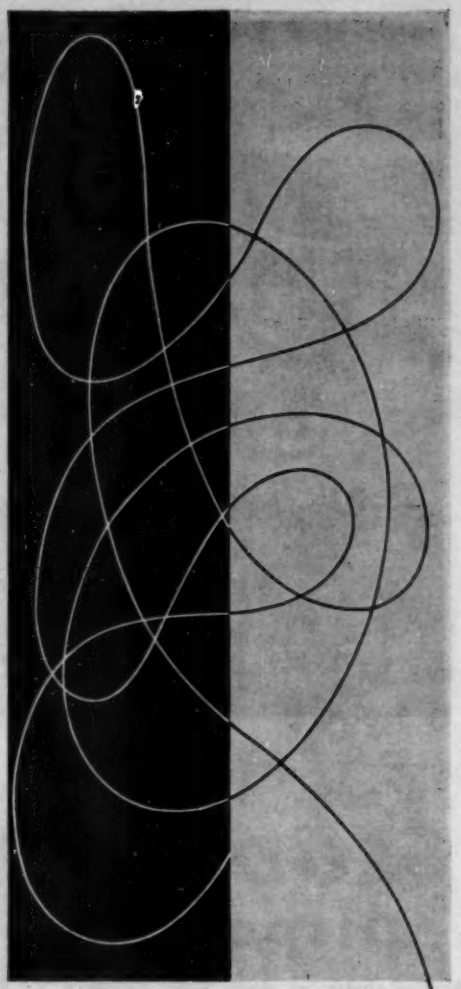

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